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# Co-production of silica from geothermal fluids

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## Disclaimer

Co-production of Silica from
Geothermal Fluids


Final Report




California Energy Commission Project
PIR-00-003

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## 1   Title Page

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## 3  Acknowledgements

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## 5   Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Energy Commission) annually awards up to $62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Building End-Use Energy Efficiency

- Industrial/Agricultural/Water End-Use Energy Efficiency

- Renewable Energy

- Environmentally-Preferred Advanced Generation

- Energy-Related Environmental Research

- Strategic Energy Research

What follows is the final report for PIR-00-003 conducted by Lawrence Livermore National Laboratory. The report is entitled "Co-production of Silica from Geothermal Fluids". This project contributes to the PIER Renewables program.

For more information on the PIER Program, please visit the Commission's web site at: http://www.energy.ca.gov/research/index.html or contact the Commission's Publications Unit at 916-654-5200.

## 6 Executive Summary

The purpose of this project was to investigate whether a cost-effective method to extract marketable silica ($SiO_2$) could be developed in order to co-produce silica at geothermal power plants. Marketable silica would provide an additional revenue source for the geothermal power industry and therefore lower the costs of geothermal power production. After discussions with staff at several geothermal sites in California, we chose to work at the Mammoth Lakes, California site operated by Mammoth Pacific L.P. (MPLP). Two main factors affected this decision. First, the geothermal fluid at this site provides an optimum opportunity to produce high-quality, high purity silica because there are few other dissolved species in the fluid. Second, MPLP could increase their summer power production by cycling the post-extraction low-silica water through cooling panels to reduce fluid temperatures downstream from the turbines. MPLP therefore has a dual use for the silica extraction process. Once developed, the silica extraction method could be readily modified for other California geothermal sites.

We tested extraction processes at Mammoth in a mobile laboratory using geothermal fluid obtained downstream from the power plant heat exchanger at 50-70°C. We treated the geothermal fluid with reverse osmosis (RO) to supply a concentrated fluid to the reactor vessel and a dilute fluid for the cooling panels. We extracted silica in two forms for different markets: precipitated solid silica, and a colloidal silica slurry. When our goal was to precipitate silica, the concentrated fluid flowed through our continuously stirred reactor where chemicals, such as salts and polyelectrolytes, were added to induce silica precipitation. Dissolved silica polymerized to form colloids, which agglomerated to form particles. The particles or unagglomerated colloids were removed downstream from the reactor in a series of ultra-filtration membrane tubes. When our goal was to produce a colloidal silica slurry, colloids were concentrated from the fluids without inducing agglomeration.

The degree of concentration in the RO unit was tuned to provide the optimum silica concentration for extraction. The flow rate through the reactor was adjusted to optimize the fluid residence time. Process variables used to tune silica properties included the concentration and type of additive, residence time of the fluid in the reactor, pH, and filtration method. The silica by-product was further characterized at LLNL, and sent to outside laboratories for market tests.

We have shown that we can produce marketable silica by-products, both as a solid precipitate useful in rubber binder applications, and a colloidal slurry useful in precision casting and paper applications. The market value of silica that could potentially be produced from the Mammoth Lakes site if the

entire fluid stream is used for silica extraction is about $11,000,000/year based on a typical market price of $0.75/lb. for precipitated silica used in rubber manufacture and a silica recovery of 7200 tons per year[1].  For a process that treats and extracts silica from a volume of fluid stream sufficient only to provide a low-salt fluid for use in evaporative cooling panels (~1.1 mgd), the estimated capital cost for the extraction technology we have identified is about $2,300,000 with operating costs of about $700,000 per year.  The value of silica produced is $900,000. These preliminary estimates suggest a rate of return of 14% and payout in 7 years.

These estimates are highly preliminary, however.  We believe that uncertainty in the economics of silica extraction has been the major impediment to the commercialization of silica co-production.  Pilot testing will be required to optimize the design of a silica extraction system and to validate that design by long-term testing.  Data from the pilot tests can then be used to rigorously determine the economic feasibility of commercial silica extraction at the Mammoth Lakes site.

## 7    Abstract

The purpose of this project was to develop a method for extracting silica from dilute (1300 ppm TDS) geothermal fluids with 250 ppm dissolved silica at the Mammoth Lakes, California geothermal plant. Our process used reverse osmosis (RO) to concentrate the silica up to 1000 ppm to enhance the silica polymerization/agglomeration process. The fluid (RO concentrate) then entered a stirred reactor where silica precipitation was encouraged through several methods including cooling, the introduction of additives, and pH adjustment. Additives included calcium and magnesium choride salts, ammonium chloride, and proprietary compounds XP-251 and XP-252 from ChemLogis Inc. Silica particles were captured in 200 nm cartridge filters, and later in 50 nm cross-flow ultrafilters. Best silica yields were obtained by using additive XP-251 combined with pH adjustment to pH 8.5 using sodium hydroxide. The solids were 98% $SiO_2$, the major impurities being $Na_2O$, $Al_2O_3$, and $Fe_2O_3$. A distilled water rinse removed most of the sodium. Dilute acid removed most of the other components and resulted in silica having 99.6 % purity. Colloidal silica was also captured in extraction tests using cross-flow ultrafiltration.

Both precipitated silica and colloidal silica are marketable by-products for the Mammoth Lakes fluid. Because no additives are needed to generate colloidal silica, it is the preferred by-product for subsequent silica extraction work at this site. A preliminary economic analysis suggests the process will have a 14% rate of return with payout in 7 years.

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[1]  Projections for marketing colloidal silica yield similar estimates because of similar market prices for solid and colloidal slurry by-products when normalized to grams of silica.

## 8  Introduction

### 8.1  Background and Overview

This goal of this project is to make geothermal energy, a renewable energy source, more competitive by developing a method for co-producing marketable by-products from the geothermal fluids. Numerous valuable mineral commodities exist in geothermal fluids,  that, if extracted in marketable form, can greatly increase the profitability of geothermal power production. Potential by-products common in geothermal fluids include silica, lithium, tungsten, bromine, iodine and cesium.

#### 8.1.1  Previous work on silica extraction from geothermal fluids

There have been previous attempts to commercialize silica extraction from geothermal fluids.  The Caithness Dixie Valley geothermal site extract a precipitated silica for markets that they have not revealed for reasons of business sensitivity[2].  The Dixie Valley fluid is slightly more alkaline and has a slightly higher silica content than the Mammoth Lakes fluids.

The most successful silica extraction technologies have been developed in New Zealand by Kevin Brown, James Johnson, and co-workers.  Brown has developed a colloidal silica extraction process with which he can control silica colloid size[3].  It has been difficult to find a market for this material because of the remote location of the Wairakei geothermal site in central North Island of New Zealand.  Transportation is a significant component of the production cost.

Johnson has developed a method for extracting silica useful for a paper additive at New Zealand's Kawerau geothermal site[4].  For a while the silica was being used at the nearby Tasman pulp and paper mill, but the use was discontinued because of a decreasing demand for that type of paper.

Other workers, particularly in Japan and Russia, are actively pursuing silica extraction from geothermal systems.  However, as of yet, no commercial marketing has been achieved.

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[2] Lin, Mow and others (2003) Recent advances in the development and commercialization of geothermal silica products. Geothermal Res. Coun. Vol 27, p. 547-550.

[3] Brown, K., and Bacon, L. G (2000) Manufacture of silica sols from separated geothermal water. Proc. World Geothermal Congress.

[4] Harper, R. T. and others (1995) An integrated approach to realize greater value from high temperature geothermal resources: A New Zealand example. World Geothermal Congress, v 4, p. 2853-2858.

## 8.2   Project Objectives

The objective of this project is to develop a silica ($SiO_2$) extraction procedure for specific geothermal power plants that is ready for pilot-scale testing.  The procedure will produce an optimized silica by-product with characteristics that match those of known commercial silicas.  The precipitation method we develop will be optimized to minimize chemical costs, energy use, labor, and capital expenses such that the sale of silica results in a new positive revenue stream for the plant.

The projected benefit will be a marketable silica by-product having a value between ten cents and two dollars per pound.  By providing an additional revenue stream from the sale of a marketable silica by-product, success of the current project will lead to lower geothermal energy production costs.  It also may allow sub-economic geothermal resources to be developed where power production alone would not be economic, and in so doing increase the amount of geothermal energy production in California.  Furthermore, because silica removal decreases scaling in the power plant and re-injection lines, project success would also decrease substantially the costs associated with scale removal.  Decreasing the overall scaling potential would allow additional geothermal energy extraction in bottoming cycles, or additional uses of low-grade heat that are currently prohibited due to scaling problems. It would also allow downstream extraction of other metals such as lithium, for which silica scaling is currently an obstacle.

## 8.3   Report Organization

This report is organized by first presenting our project approach, which is an intended scope of work needed to accomplish our project objectives. This is followed by a detailed description of our project outcomes, which includes the results of our silica extraction tests at the Mammoth Lakes geothermal site, results of laboratory work to analyze and characterize the silica by-product, and a preliminary economic analysis for silica extraction at Mammoth Lakes. We conclude with recommendations for further work needed to implement a silica extraction process at the Mammoth Lakes geothermal plant, and a discussion of how silica extraction at Mammoth Lakes is related to silica extraction at other geothermal sites.

## 9   Project Approach

## 9.1   Project Organization

This project is broken down into three technical subtasks defined below. These descriptions are taken verbatim from the project work scope.

*Subtask 2.1.1  Laboratory testing of precipitation process variables*

Prior to field testing, LLNL will perform a limited number of silica precipitation laboratory tests using simulated geothermal fluids.  The purpose of these tests is to determine the overall rate of silica precipitation for a given precipitation process (such as cooling, pH change, or salt addition), and the properties of the resulting silica precipitates.  This information is used to estimate needed residence times for the tank reactors and prioritize the precipitation methods to be field tested, and to design the field experiments.  This information is vital to defining the working parameters for pilot-scale tests.

The silica precipitation tests consist of making up silica-rich salt solutions that mimic the compositions of fluids at selected geothermal sites.  The compositions are based on solution analyses of geothermal fluids provided by the site operators.  The fluid is placed in a heated stirred reactor and silica precipitation is induced at the temperature of interest using one or a combination of three methods: salt addition, pH change, and cooling.  The silica precipitates are removed and characterized using one or more methods.  Scanning electron microscopy (SEM) is used to measure particle sizes and examine the textures of the silica agglomerates.  Gas adsorption surface area measurement (BET) is used to determine silica surface area, a key characteristic for industrial uses.  Dynamic light scattering (DLS) is used to measure particle size and size distribution for suspended silica colloids.  X-ray diffraction (XRD) is used to identify any crystalline co-precipitates.  Emission spectroscopy (ICP-AES) is used to determine the chemical composition of the precipitates.  The chemical composition is important because one of the concerns with geothermal silicas is that they may contain significant amounts of contaminants such as iron, arsenic, calcium, and others.  These contaminants may affect the properties and toxicity of the silica and make it less attractive for industrial use.

*Subtask 2.1.2  Field tests of precipitation processes*

The main goal of this subtask is to study how a marketable amorphous silica can be produced from spent geothermal fluids under actual field conditions.  At each site, LLNL will tap into spent geothermal fluids at the appropriate point in

the production line and use the silica precipitation methods listed above (salt addition, pH adjustment, temperature drop) to generate amorphous silicas. LLNL will have prepared a test matrix of conditions to be used to generate the silicas. The matrix will be designed to systematically vary precipitation conditions and trap a representative sample of silica for each set of conditions. The previously performed laboratory tests (from subtask 2.1.1) will be used to construct the test matrix. For field tests the produced silica is trapped in an ultrafiltration membrane module. The module allows the silica sample to be preserved as a wet paste, as preferred. A new filter will be swapped in for the next set of precipitation conditions. The trapped silica in the filters will be returned to LLNL for characterization using the same methods described in Subtask 2.1.1. In addition, silica samples will be sent out to commercial laboratories as described in Subtask 2.1.3 below. Up to 800 grams of silica will need to be generated in some of these tests in order to have enough material for full-scale tire rubber testing. That need will be reflected in the design (flow rate, residence times) of the field equipment.

*Subtask 2.1.3  Post-processing and testing of silica in industrial uses*

In this Subtask, silica extracted from field and laboratory tests will be post-processed (rinsed, leached, dried etc. as necessary) and sent to industry consultants. The consultants will test the silicas for use in specific silica applications, report on their performance, provide advice on required silica properties, and help to define appropriate commercial silica markets for geothermal silicas.

Post-processing consists of leaching, washing, and drying of the precipitated solids if required to produce commercially useful silica. As initially obtained from the reactor, amorphous silica may be contaminated with varying amounts of impurities such as arsenic, iron, and calcium. Leaching and washing will be studied with respect to the composition of leachant, use of surfactants, temperature and mechanics of leaching, and the purity and microscopic surface characteristics of the silica produced.

In addition to the leaching and washing processes, the amorphous silica must eventually be dried to a form suitable for subsequent use. During this process and the preceding leaching/washing operations, a critical microscopic

characteristic of the amorphous silica that must be
maintained is its open structure, which gives the material
high surface area and porosity.  Several methods for drying
powders on a large scale, such as spray drying, are
available, and will be evaluated for use with the amorphous
silica.  Milling of the dried amorphous silica may also be
needed to obtain amorphous silica of the required particle
size.  This work will focus on recovering the amorphous
silica of the required particle size and porosity, and extensive
use will be made of the measurement
techniques of fine particle technology to try to correlate the
particle properties of the amorphous silica with its suitability
for the desired applications.

The silica will then be sent to collaborators for testing for
specific applications. John Byers of Byers Rubber Consulting
will be our consultant to determine how our produced silicas
can be optimized for use in the rubber industry.  Byers will
test the produced silicas as rubber additives.

## 9.2   Selection of field site

(*The work described here relates to Subtask 2.1.2 of PIR-00-003.*)

Our original plan was to work at two geothermal sites.  In addition to
Mammoth Lakes, the other preferred site was Caithness Operating
Company's Coso site, or alternatively, CalEnergy's site at the Salton Sea.
However, neither site operator allowed us access for silica extraction work.
Caithness stated that they are carrying out proprietary silica extraction work
at Coso and did not want collaborators on this work (although they are
receptive to carrying out our DOE-funded work on silica anti-scalants at their
site).  At the time of initiation of this project, CalEnergy expressed interest in
a collaboration, but preferred to wait until their zinc extraction process was
on line and stable.  Since that time, CalEnergy has terminated most of their
work on zinc extraction and does not appear to be interested in further
minerals recovery at this time.  For these reasons, we have devoted all our
efforts to date on work at the Mammoth Lakes site.  The staff at Mammoth
Pacific have been very generous in supporting this work by providing
geothermal water, power, logistical support of all kinds, approximately 20
man-days of technical support, and unlimited site access.

We began our site work at the Mammoth Lakes geothermal site in June of
2002. After two site visits to Mammoth Lakes during which silica extraction
was unsuccessful (see section 3.3 below), we discussed further options with
California Energy Commission staff.  We could remain at Mammoth Lakes

and continue our efforts, or abandon work at Mammoth Lakes and renew our attempts to get site access and begin work at a new geothermal site. Several factors led us to decide that the best use of funds would be to remain at Mammoth Lakes. We strongly believed we could incorporate reverse osmosis processing to extract silica successfully. The use of reverse osmosis to enhance silica extraction yields a low salt, low silica by-product that is ideal for Mammoth Pacific's need for a fluid to cycle through their evaporative cooling panels. This dual use for our technology combined with the high purity of the fluid make the Mammoth Lakes site ideal for economic silica extraction. Thus we felt the best chance of project success was to remain at Mammoth Lakes and not switch to a new site. A more detailed discussion of favorable geothermal site attributes for silica extraction is included in Section 11 below.

This California Energy Commission-funded project benefited from funding received by Lawrence Livermore National Laboratory (LLNL) from the DOE Geothermal Technologies office. In years previous to the start of this project, the DOE funding to LLNL was targeted at extraction of silica and other metals from hypersaline brines at CalEnergy's Salton Sea site that until recently were being mined for zinc. Laboratory tests and computer simulations were carried out at LLNL in order to identify methods for cleaning the high iron silica removed from the geothermal fluid upstream from their ion-exchange zinc extraction process. Some methods were developed and tested in the laboratory, but this work is on hold pending renewed interest by CalEnergy. Cleaner silicas could be marketed, whereas the impure silicas produced at 100 tons per day are currently discarded to a local landfill. Some of the silica extraction and characterization methods developed for the Salton Sea work have been modified and used in our Mammoth Lakes project.

## 10  Project Outcomes

(*The work described here relates to Subtask 2.1.2 of PIR-00-003.*)

### 10.1  Summary of results

This project has focused on silica extraction from geothermal fluids at Mammoth Pacific L.P.'s binary plant at Mammoth Lakes, California. The geothermal fluids have low total dissolved solids (TDS) of about 1300 ppm and low silica content (~250 ppm) (see Table 1). The fluid source used for our silica extraction is taken downstream from the heat exchanger and ranges from 50 to 70$^{\circ}$C seasonally (Figure 1). Low salt content and low trace metals make this fluid ideal for extracting a high purity silica by-product.

**Table 1**.  Composition of Mammoth geothermal fluid in mg/ L sampled from downstream of the heat exchanger (Geothermal Fluid Comp.) and after RO processing (concentrate and permeate).

|  | Geothermal Fluid Comp. | Reverse Osmosis Products | |
| --- | --- | --- | --- |
|  |  | Concentrate | Permeate |
| Sodium | 345 | 705 | 24 |
| Potassium | 33 | 65 | 2 |
| Silica | 255 | 645 | 18 |
| Aluminum | 0.25 | 0.27 | 0.15 |
| Magnesium | 0.21 | 0.37 | 0 |
| Lithium | 1.9 | 3.8 | 0.1 |
| Calcium | 2.1 | nd | 0 |
| Chloride | 235 | 501 | 1.4 |
| Sulfate | 116 | 224 | 1 |
| Iodide | 0.3 | 0.9 | 0 |
| Bromide | 0.5 | 1.1 | 0 |
| Fluoride | 12 | 23 | 0.4 |
| Strontium | 0.14 | 0.3 | 0 |
| Rubidium | 0.3 | 0.6 | 0.02 |
| Cesium | 0.3 | 0.7 | 0.02 |
| Tungsten | 0.2 | 0.4 | 0.003 |
| Arsenic | 1.3 | 2.8 | 0.04 |
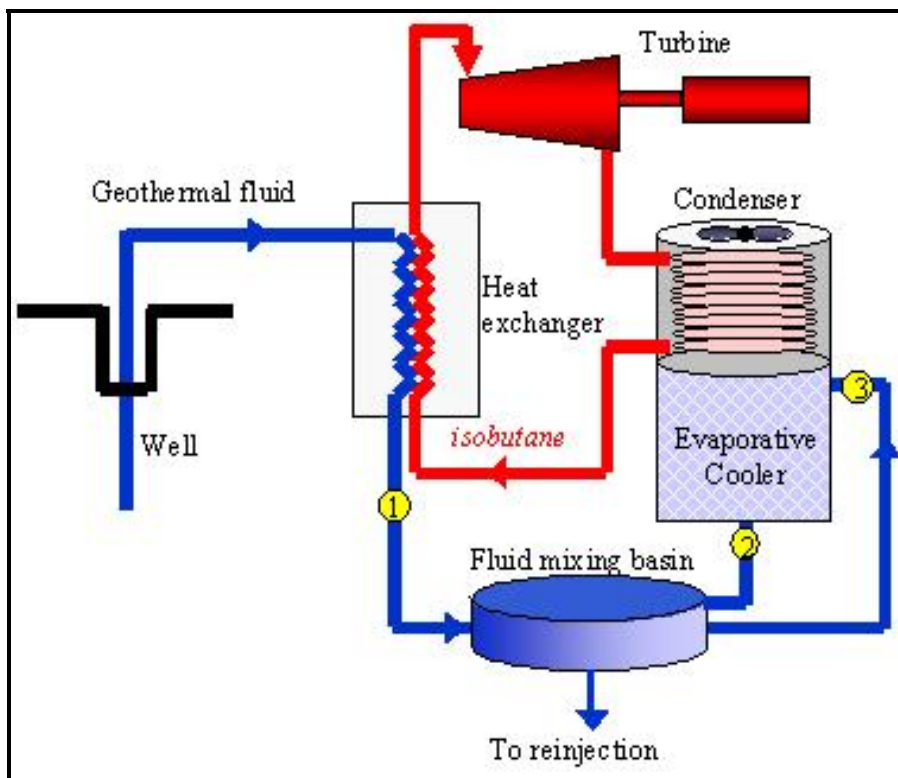
**Figure 1**.  Schematic of Mammoth binary plant showing where fluids were sampled for silica extraction (yellow dots):  1) June 2002; 2-3) July 2002.

Although there is presently not a silica scaling problem at the plant, there is a need for a low silica, low salt water for use in evaporative cooling panels now installed in the two 5 MW pilot plants, and potentially to be installed in the two 15 MW main power plants.  Silica extraction from spent geothermal fluid would provide a suitable fluid source for cooling, eliminating the need to purchase fresh water from a local source, and would generate a new net revenue stream from the marketable silica by-product (see 10.5.4).

We have been successful in developing a working silica extraction method from the Mammoth geothermal fluids (see Figures 2 and 3).  Our process uses reverse osmosis to concentrate the silica as discussed below in section 10.4.  The Mammoth geothermal fluids are nearly ideal for reverse osmosis treatment for two reasons:  1) there is little likelihood of carbonate scaling of the membranes given the very low concentration of calcium and other divalent ions in the fluids; and 2) the lack of dissolved organics in the fluid indicates very little membrane fouling potential.  Reverse osmosis is beneficial because it makes silica extraction more efficient in terms of decreased reaction time and decreased amounts of necessary additives when compared to extraction without concentration.  In addition, the reverse osmosis unit provides a low salinity fluid with ideal characteristics for use in the evaporative cooler.  The chronology of site testing below explains how

we arrived at the need for reverse osmosis treatment and explains how our silica extraction methods are applicable to other systems.

Process variables used to tune silica properties include the concentration and type of additive, residence time of the fluid in the reactor, pH, and filtration method.  These variables are interrelated.  For example, shorter residence times produce smaller silica particles that are more difficult to filter efficiently.  Longer residence times and higher additive concentrations produce more firmly agglomerated particles that are relatively easy to filter, but they have lower surface areas and pore volumes, and may not be suitable for high-end commercial applications such as paper and tire fillers.
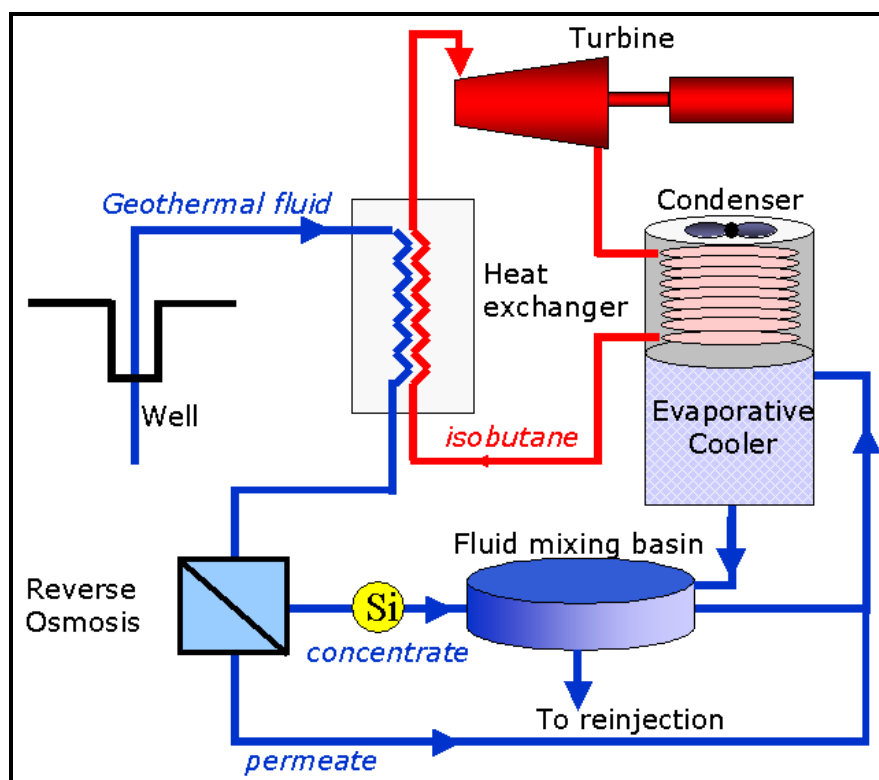


**Figure 2.**  Schematic of location of reverse osmosis unit relative to fluid flow through geothermal plant. Silica is extracted from reverse osmosis concentrate (yellow dot labeled Si). When in production, the permeate would feed the evaporative cooler.  The silica extraction step is expanded in Figure 3.
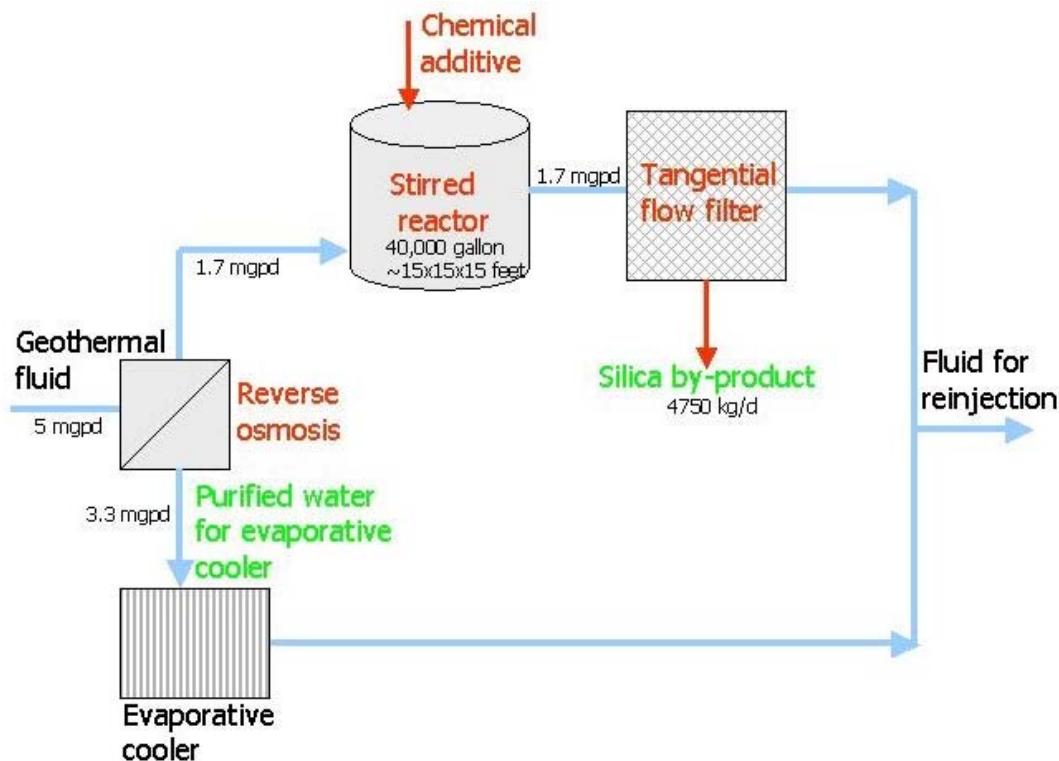
**Figure 3.** Schematic showing flow paths for reverse osmosis and silica extraction systems. Flux vales are for hypothetical 5 MGD input stream.

## 10.2  Results of laboratory tests with simulated fluids

(*The work described here relates to Subtask 2.1.1 of PIR-00-003*.)

Prior to beginning field work, we carried out tests of silica extraction from synthetic fluids having similar chemistries to the target geothermal fluids. We generally added components that occurred in the millimolal range or higher, and ignored trace and minor elements in these tests.  The purpose of these tests was to provide a general idea of the rates of silica polymerization and agglomeration so that we could then design our field equipment with the correct characteristics.  For example, silica polymerization rates are a function of temperature and the degree of silica supersaturation.  They are also a function of cation concentrations in the solution.  High calcium, magnesium, and iron concentrations, for example, increase the silica polymerization rates.  For this reason, the fluid must be 'aged' for enough time to allow silica precipitates to grow.  Therefore the flow rate and size of stirred reactor must be appropriate for the residence time needed for silica growth.

10.2.1 Polymerization rates

Because of the low silica concentration and low salinity of the Mammoth Lakes fluids, silica polymerization rates are very slow. Appendix 13.1 provides details of laboratory and field tests illustrating this point. Overall, appreciable silica polymerization took on the order of hours to days. Such long times periods would necessitate a very large reactor to allow sufficient residence time for silica polymerization and agglomerization to take place. In the aforementioned tests, additives such as magnesium chloride, calcium chloride, and ammonium chloride were used. In some the tests, the pH was raised to 9 to increase the polymerization rate. In other tests, silica nuclei were added to act as nucleation sites for silica growth. In all of these tests, the rates were still too slow to be economic at a geothermal site.

A series of tests were then carried out with elevated silica concentrations to see how high silica concentrations should be in order to achieve relatively rapid polymerization (a few minutes to half an hour). As shown Figure 4, polymerization rates are fairly rapid with silica concentrations of approximately 600 ppm.
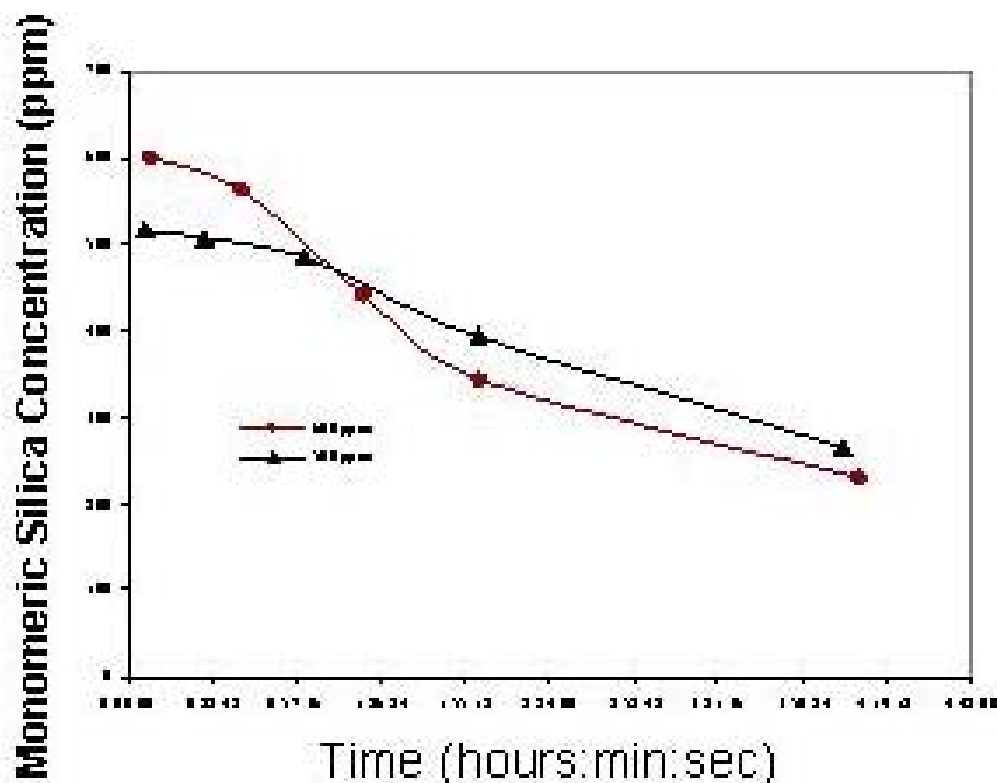


**Figure 4.** – Polymerization of silica in synthetic Mammoth Lakes brine at elevated silica concentrations. Monomeric silica decreases in time as silica polymerizes to form polymeric silica. The rate of decrease of monomeric silica therefore indicates the rate of formation of polymeric silica. With continued polymerization, the silica forms

colloids. The rate of polymerization is important because fast polymerization allows shorter processing times and therefore lower production costs.

10.2.2 Implications for field tests

It is clear from these tests using synthetic fluids that silica concentrations should be higher to achieve more rapid silica extraction. However, given that these are synthetic fluids, and not real fluids, we decided to carry out a set of field tests to determine whether or not other factors, such as residence time in the heat exchanger, the presence of nuclei in the fluid, or the existence of minor components in the real fluid and not in the synthetic fluids could be significant. We also tested samples from one of the hottest wells in the field that had about 300 ppm silica in hopes that the silica in this fluid would polymerize more rapidly. We also tested fluids downstream from the evaporative cooling panels, that had cooled and had significantly more time for silica to polymerize than the fluids taken directly from the heat exchanger. However, none of these fluids showed significantly more rapid silica polymerization than our original test solutions, as described in more detail in Appendix 13.1.

10.3  Construction of apparatus for field tests of silica extraction

With the information collected during the laboratory experiments, we assembled extraction equipment based on the use of a previously-purchased 20 liter stirred reactor (using DOE funds). The reactor had ports available for pumping in additives. Pleated filter cartridges (200 nm) were used to filter out silica downstream from the reactor. Metering valves, flow meters, pressure relief valves, thermocouples, and plumbing for a fluid by-pass line were added to the system as needed. The unit was housed in a trailer to allow subsequent use at other geothermal sites. Figure 5 shows this equipment.

10.4  Chronology of field testing

(*The work described here relates to Subtask 2.1.2 of PIR-00-003*.)

Prior to installing the RO unit to concentrate the silica, an extraction system capable of processing about 1 gallon of brine per minute was designed and constructed. The system uses as its core a 5-gallon (20 liter) stirred reactor. The pH and ionic strength of the fluid in the reactor are monitored by a computer, which allows for convenient control of the pH and salt content of the fluid during a given experiment. This computer also controls the pumps that input additives to induce and control silica precipitation. The input, output, and sampling ports of the reactor have been modified to interface with site facilities.

**Figure 5**.  Twenty liter stirred reactor used to carry out silica precipitation tests in our on-site mobile laboratory.

10.5  Chronology of field testing

(*The work described here relates to Subtask 2.1.2 of PIR-00-003*.)

Prior to installing the RO unit to concentrate the silica, an extraction system capable of processing about 1 gallon of brine per minute was designed and constructed.  The system uses as its core a 5-gallon (20 liter) stirred reactor. The pH and ionic strength of the fluid in the reactor are monitored by a computer, which allows for convenient control of the pH and salt content of the fluid during a given experiment.  This computer also controls the pumps that input additives to induce and control silica precipitation.  The input, output, and sampling ports of the reactor have been modified to interface with site facilities.

After some initial laboratory silica extraction tests using simulated Mammoth fluids, we began our site work.  Extraction tests carried out the first week (June 2002) confirmed the results of our initial lab tests:  silica polymerization was too slow, such that residence times of days to weeks would be needed to get sufficient silica polymer growth to enable agglomerating agents to produce visible precipitates. Samples were taken from point labeled 1 in Figure 1 for these tests.

During our second site visit (July 2002) we attempted to precipitate silica from fluids taken upstream and downstream from the evaporative cooling panels (labeled 2 and 3 in Figure 1).  These fluids have cooled to ambient conditions and have had a longer period for silica polymerization to take place.  Both effects should enhance silica precipitation via salt addition. However, little silica precipitation could be induced, and the fluids contained large amounts of airborne debris that would need to be removed from the silica precipitate for most uses.  During this field session, we also sampled

and tested one of the hottest (and highest silica) wells for silica extraction. Even when the silica concentration approached 300 ppm silica, we did not produce significant amounts of silica precipitate from the untreated geothermal fluids.

During these tests, we used several inorganic salts ($MgCl_2$, $CaCl_2$, $Ca(OH)_2$ and $NH_4Cl_2$) and also two commercial chemical products supplied by Mark Stapleton of ChemLogis (XP-251 and XP-252) to induce silica preciptiation. None of these additives were able to induce silica precipitation in the fluids in less than several hours. Of these, XP-251 was most effective.

At this point, we decided it was necessary to concentrate the Mammoth fluid for silica extraction and chose to use high temperature reverse osmosis (RO) to do this. A portable 8 gpm RO unit was leased from Osmonics Corporation (now GE-Osmonics) using our DOE matching funds. In October 2002, the RO unit was installed upstream from our stirred reactor and was used as the initial step in processing the geothermal fluid (see Figures 2 and 3). The RO unit produced a low TDS, low silica "permeate" fluid suitable for the evaporative cooler, and a silica-enriched higher TDS "concentrate" fluid for silica extraction (see Table 1). RO process conditions were adjusted to produce fluids that could be selectively varied to have silica concentrations of 500 to 800 ppm. Silica extraction from these fluids was rapid because of higher silica and background salt contents. Typical residence times in the stirred reactor were 5-30 minutes. No indication of fouling of the RO membrane was observed in these tests (fouling would cause the throughput to decease for a given pressure gradient across the RO membrane). RO was used in all subsequent extraction tests carried out in this project.

Silica precipitates were collected in 0.2 micron (200 nm) cartridge filters downstream from the stirred reactor. The filters have proven to be only marginally effective in capturing the silica, in spite of the measured particle size for precipitated silica particles of several microns determined on-site using dynamic light scattering (DLS). The particles apparently deform and squeeze through the filter pores. In later field tests we replaced the cartridge filters with cross flow ultrafilters of finer pore size (as small as 50 nm) to improve silica collection efficiency and to collect the finer grain size fraction.

In order to increase the amount of silica by-product, we purchased a larger stirred reactor in which to carry out the precipitation tests (using DOE matching funds, Figure 6). Some marketing tests need kilogram amounts of silica, whereas we currently produce only a few grams per hour. The new reactor volume is 80 liters, four times the size of our previous reactor. The reactor was built to our specifications by Pressure Products of Charleston, West Virginia. It was then coated with "Curralon," a polyphenylene sulfide

(PPS) polymer developed at Brookhaven National Laboratory for use in preventing corrosion in geothermal applications.  The Curralon allowed us to use low-alloy, and therefore inexpensive, 12" iron pipe for our reactor.



**Figure 6**. Eighty liter PPS coated stirred reaction vessel custom built for our silica extraction work.  The vessel has 12 I/O ports for sampling, additive injection, temperature, or pressure readings. The vessel is rated up to 100 psi and 100$^{\circ}$C.

We also purchased a used 25 gpm (94 lpm) reverse osmosis unit (using our DOE matching funds) that uses up to six 8" x 40" reverse osmosis membrane elements.  We modified the unit extensively (Figures 7 and 8). We replaced all PVC tubing with high temperature (C-PVC) tubing to allow us to use the unit up to 80$^{\circ}$C.  We added connections to allow the permeate to be stored in ~750 L tanks for later use to flush the reverse osmosis membranes.  We also provided plumbing to connect the concentrate line as feed to our new stirred reactor, and then to an ultrafilter for downstream silica collection.  The combination of larger volume reactor and higher flux RO unit allowed us to process up to 10 liters per minute of brine and extract up to 150 grams of silica per hour.
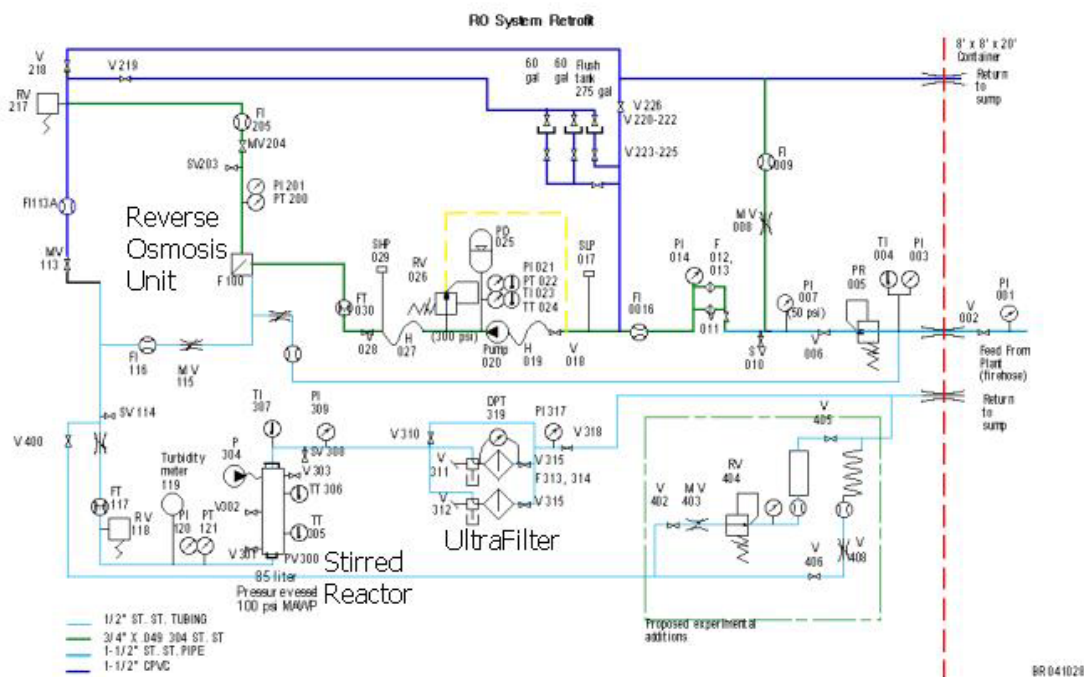
**Figure 7**. Schematic of reverse osmosis-stirred reactor-ultrafiltration system for silica extraction.  System is designed to allow a wide range of silica concentrations and fluid residence times in the reactor to allow silica extraction tests over a wide range of conditions.



**Figure 8**. Plumbing, flow metering valves, and diagnostic equipment associated with the reverse osmosis unit. Concentrate by-pass flux is controlled with the special flow-control valves (blue tops) to allow precise control of silica concentration in the concentrate.

The 80 liter reaction vessel, the 94 lpm RO unit, two 225 liter tanks, and one 750 liter tank were installed into a 20 ft. cargo container (8 ft. x 8 ft. x 20 ft.) and used to extract silica in our final field tests carried out in December 2004. These tests targeted a colloidal silica by-product and thus did not require the addition of any agglomerizing chemical agents to the stirred reactor. Results of these field experiments are presented in Appendix 13.2. To summarize: The fluid taken from downstream of Mammoth Pacific's heat exchanger was plumbed into the cargo container and typically entered the extraction system at a temperature of ~70°C and a pressure just under 130 psi. The fluid immediately was forced through a pressure reducer that was set to 45 psi to accommodate the pump used to circulate the fluid through the RO unit; the next step was pumping the fluid through the RO unit. The concentrate coming off the RO unit flowed into the bottom of the stirred reactor, filling the vessel from the bottom, and after the vessel was filled the fluid would flow from connections at the top of the vessel into a tubular ultrafilter. Initially, significant heat loss was observed as the fluid filled the reactor and then flowed into the ultrafiltration unit (the initial fluid going into the ultrafilter was ~26.7°C). However, within two hours the walls of the reactor warmed and the amount of heat loss decreased such that the average fluid temperature in the reactor reached 70°C.

We obtained ~10 liters of ultrafiltered concentrate in ~4 hours. Portions of these samples were analyzed using refractometry and hydrometry (see Section 10.5.2.5 below), while most of the samples were sent to Mark Jarand of Colloidal Solutions for market testing (see Section 10.5.3.2).

## 10.6 Properties of silica products

(*The work described here relates to Subtask 2.1.3 of PIR-00-003.*)

### 10.6.1 Chemical compositions

Table 2 highlights the composition of a silica precipitate representative of those precipitates obtained during the December 2002 field outing. The silica is very pure, as evidenced by the occurrence of 98 wt.% silica even in the untreated samples. Sodium is the largest impurity and is readily removed by either a de-ionized water or acid leach, as shown. The acid rinsed silica is 99.6% pure (rinsed for 1 minute in pH 2 HCl solution). The other impurities are all very low and are within the range of the impurity levels of commercial precipitated silicas. More compositional information on the silica precipitates and processed fluids are given in Appendix 13.3. Note the measureable concentration of arsenic (450 ppm) in the silica. Arsenic is addressed in detail below because it is a regulated toxic substance and therefore might pose a potential problem for some commercial uses of the silica precipitate.

**Table 2**. Composition of silica precipitates.

| | Raw | DI Rinse | AcidRinse |
|---|---|---|---|
| Major components in wt % | | | |
| SiO2 | 98.09 | 99.13 | 99.63 |
| Al2O3 | 0.33 | 0.31 | 0.31 |
| Fe2O3 | 0.22 | 0.22 | 0.20 |
| MnO | 0.01 | 0.01 | 0.01 |
| MgO | 0.13 | 0.12 | 0.04 |
| CaO | 0.17 | 0.15 | 0.02 |
| Na2O | 1.15 | 0.08 | 0.02 |
| | | | |
| K2O | 0.15 | 0.05 | 0.00 |
| TiO2 | 0.01 | 0.00 | 0.00 |
| P2O5 | 0.03 | 0.03 | 0.02 |
| Total | 100.28 | 100.11 | 100.26 |

| Minor components in ppm | Raw | DI Rinse | AcidRinse |
|---|---|---|---|
| As | 450 | 304 | 162 |
| Au | 0.07 | 0.06 | 0.05 |
| Cs | 21 | 18 | 5 |
| Hg | 4 | 4 | 1 |
| Mo | 20 | 18 | 10 |
| Sb | 350 | 332 | 200 |
| Sc | 0.3 | 0.3 | 0.2 |
| W | 31 | 26 | 15 |
| Cu | 14 | 13 | 10 |
| Zn | 126 | 175 | 46 |

10.6.1.1              Impurities

While the EPA does not regulate the arsenic content of precipitated or colloidal silica, various organizations do regulate the arsenic content of end-use applications of the silica products; for instance, the United States Department of Transportation regulates the amount of arsenic in tire rubber. The compliance of marketable products made with our silica products will be tested during a future Pilot study and any non-compliance will be further addressed at that point.  However, because the amount of arsenic in our silica products could negatively affect their raw market value, we investigated methods for decreasing the amount of arsenic in the silica precipitates and colloids produced from our extraction processes.  A summary of our efforts to date is provided below.

## 10.6.1.2    Methods for purification

Several approaches could be used to remove arsenic from the silica.  Our methods consisted of short duration rinsing in water and dilute acid. As seen in Table 4, about 64% of the arsenic is removed with a dilute acid rinse. Note that arsenic occurs in the geothermal brine as As(III) that subsequently oxidizes in air to As(V).  Oxidation to the arsenate ion should cause arsenic to desorb from the silica.  Both oxidation and acidification should be used in future attempts to remove the arsenic to acceptable levels, once these levels are determined by constraints imposed by the chosen silica market.

As noted above, the arsenic content of the Mammoth geothermal fluids and the resulting silica products may limit the applications of the silicas. However, about 90% of the arsenic in the fluid is not incorporated in the silica, but stays in solution.[5]  This implies that arsenic removal is best done by cleaning the silica, not by removing arsenic upstream from the silica precipitation step.

Readily available arsenic "getters" such as ion exchange resins and granular ferric hydroxide (GFH) may also be effective.  The preferred method would be to suspend the resin or GFH inside a porous bag placed inside a vessel that contains a flowing suspended silica slurry (Figure 9). The suspension would allow intimate contact between the silica colloids and the container getter material.  The getter would absorb arsenic to very low levels and effectively transfer the arsenic from the silica to the getter.  The getter could then be cleaned, and thus re-used, using geothermal fluid and the arsenic-containing waste fluid reinjected with spent geothermal fluid.  No primary or secondary waste stream would be generated with this process.

We have not pursued this method further pending a decision of which markets we will pursue. Arsenic contents of this level are not a concern for some silica applications.

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[5] To further illustrate this point, note that the silica/ arsenic ratio in the fluid is about 70, whereas this ratio in the silica precipitate ranges from about 1020 in untreated samples to about 2878 in the acid washed samples, as calculated from values reported in Table 4.
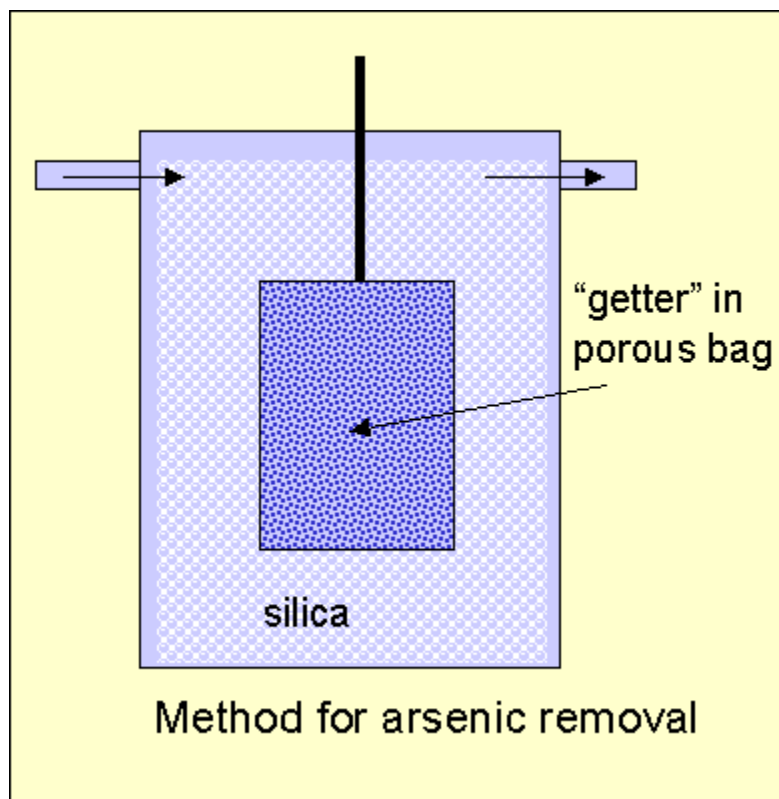
**Figure 9**. Proposed method for cleaning arsenic from silica precipitate using commercial arsenic sorber (getter) in porous bag.


10.6.2 Physical properties of silica precipitates

10.6.2.1    Scanning electron microscope (SEM) photos

SEM photomicrogrphs of precipitated silicas recovered from Mammoth Lakes geothermal fluids and dried in air at 110°C are shown in Figure 10. The precipitates are 50-80 nm agglomerates of fine silica colloids.


10.6.2.2        Drying tests

Please see Appendix 13.4 for a detailed discussion of the drying tests on precipitated silicas.  To summarize:  higher surface areas were achieved when samples were dried at higher temperatures.  Tests of the effect of pH showed that this relationship is independent of pH.  However, the samples that were treated with either an acid or a base exhibited reduced surface areas at all temperatures.
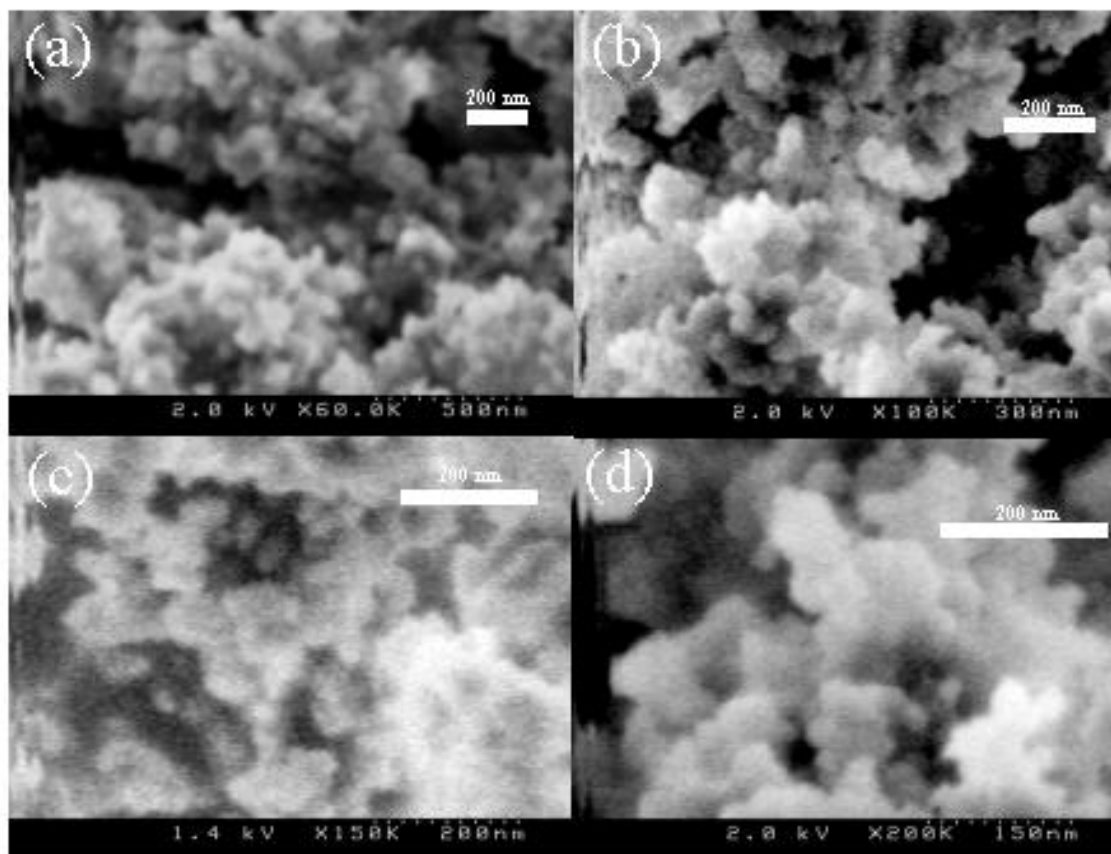
**Figure 10**. SEM photomicrographs of silica precipitates from Mammoth Lakes geothermal fluids. The silica precipitate is an aggregate of colloidal silica spheres. Scale bar is 200 nm (0.2 microns) in all photos. Photomicrograph appears poorly focused due to sample charging.

10.6.2.3            Surface area measurements

Gas adsorption is the most widely available and utilized method for determining silica surface area and pore size distribution. In this technique a gas, usually nitrogen, at its boiling point, is adsorbed on the solid sample. The amount of gas adsorbed depends of the size of the pores within the sample and on the partial pressure of the gas relative to its saturation pressure. By measuring the volume of gas adsorbed at a particular partial pressure, the Brunauer, Emmit and Teller (BET) equation gives the specific surface area of the material. At high partial pressures, where there is hysteresis in the adsorption/desorption curves (called "isotherms"), the Kelvin equation gives the pore size distribution of the sample. Gas adsorption methods are generally applicable to pores with diameters between 10 and 300 nm (mesopores).

The surface areas of our silicas varied from 40 to 130 m$^2$/g (Table 3) according to the nitrogen gas adsorption (BET) method.  For comparison, commercial precipitated silicas used in tire rubber have surface areas of 100-200 m$^2$/g.  Our surface areas are probably lower than what is representative for the actual silica because we did not capture much of the finer grain sized material in our pleated cartridge filters during the tests from which these data were obtained.

**Table 3**. Gas adsorption surface area measurements for silicas precipitated from geothermal fluids at Mammoth Lakes.  Triplicate measurements are shown for several additive concentrations carried out in beaker tests, and for three precipitated silicas produced in the reactor

| | BET Surface Area Results | | | |
|---|---|---|---|---|
| | **Sample** | **Run** | **Surface Area (m2 / g)** | **Average Surface Area (m2 / g)** |
| **Beaker Tests** | 50 ppm XP-251 | 1 | 113.72 | 114.15 |
| | | 2 | 114.18 | |
| | | 3 | 114.56 | |
| | 100 ppm XP-251 | 1 | 127.84 | 128.13 |
| | | 2 | 128.18 | |
| | | 3 | 128.37 | |
| | 200 ppm XP-251 | 1 | 106.43 | 106.53 |
| | | 2 | 106.67 | |
| | | 3 | 106.48 | |
| **Precipitated in Reactor** | Clean SiO2 | 1 | 65.96 | 65.68 |
| | | 2 | 65.57 | |
| | | 3 | 65.51 | |
| | Dirty SiO2 | 1 | 69.75 | 69.90 |
| | | 2 | 70.06 | |
| | | 3 | 69.90 | |
| | 12/13/02 9AM pH = 7 | 1 | 41.04 | 41.00 |
| | | 2 | 40.93 | |
| | | 3 | 41.03 | |
| | 12/13/02 3AM pH = 8 (NaOH) | 1 | 48.60 | 48.79 |
| | | 2 | 48.92 | |
| | | 3 | 48.85 | |
| | 12/12/02 9PM pH = 9 (NH4OH) | 1 | 57.50 | 57.75 |
| | | 2 | 57.76 | |
| | | 3 | 57.98 | |

10.6.2.4         Particle size (DLS) analysis

Dynamic light scattering (DLS) was used in the field to measure particle size of precipitated silicas.  DLS uses scattered laser light to determine the effective size of particles.  The method takes advantage of the fact that small particles scatter light with a different average direction than larger particles.  This effect is quantified in the "correlation algorithm" from which average particle sizes can be estimated.

The measured particle sizes in our silica precipitation tests generally ranged from 1-10 microns, consistent with our SEM results (Fig. 10).  These aggregates apparently were easily fragmented in the cartridge filters as they readily passed through these 0.2 micron filters.  The amount of silica trapped in the filters was determined by measuring total silica both upsteam and downstream from the filters; the net difference corresponds to the amount captured by the filter.  The amount of total silica downstream was generally only about 5% lower than the fluid upstream of the 200 nm pleated cartridge filters.

We were unable to detect unagglomerated colloidal silica particles using DLS.  The very small density difference between silica collolds and water is unfavorable for light scattering measurements.

10.6.2.5         Refractometry and Hydrometry of colloidal solutions

Refractometry and hydrometry are two techniques that were used to judge the effectiveness of the ultrafilter to concentrate the silica colloids in solution.  For our purposes, refractometry is a technique used to measure the degree to which a liquid refracts light that is passing through it, known as the liquid's "refractive index (RI)."  The RI of water is n=~1.33.  (Note that RI values are unit-less numbers denoted by "n.")  When a liquid has a higher RI than pure water, the liquid is more dense.  Thus, we expected to see the RI of the ultrafilter concentrate to increase with time as the silica became more concentrated.  The results are summarized in Table 13.2-2 and 13.2-3 of Appendix 13.2.  We did, in fact, observe a qualitative increase in the RI values of the ultrafiltered concentrate relative to the incoming fluid and the RO permeate; however, the values were below the minimum value of quantitative certainty for the refractometer and thus the actual values are not reported here.

 In later work we centrifuged samples of fluids containing colloids that were returned to LLNL from the field. After centrifugation at 14,000 g for several hours, we were able to enrich the sample to about 2 wt. % silica colloids based on a density increase of about 5 %. Samples of the colloidal solutions were then sent to a laboratory at Emory University for imaging with

transmission electron microscopy. Imaging results were not available as of the date of this report.

Hydrometry is a convenient method for determining the density of a liquid. Like the refractive index, the density correlates with the concentration of suspended silica colloids.  The hydrometer is simply immersed into a volume of slurry and the density of the solution is determined based on how high the mercury-filled bulb floats in the liquid.  For our experiments, we did notice a slight increase in the specific gravity of the ultrafiltered concentrates relative to the feed water and the RO permeate (see Table 13.2-3 in Appendix 13.2).  However, equipment problems while on-site prevented us from concentrating samples above about 1 wt %.

### 10.6.2.6 Surface titration results

For a colloidal silica solution of known concentration, it is possible to determine the average particle size using a standard acid-base titration.  As NaOH is added to a colloidal solution, some of the hydroxide is consumed by forming surface complexes on the surfaces of colloidal $SiO_2$.  With more surface area, more base (OH-) is neutralized.  Consider two colloidal silica solutions of equal wt. % silica but with one having a much larger particle size.  This solution will neutralize much less base than the solution with smaller particle size because its silica colloids have a much smaller surface area.  This effect has been quantified and used routinely to measure colloid sizes.  Details of the method are given below.  Because of budget and time constraints, these particle size analyses have not been carried out on the colloidal slurries obtained during the December 2004 field tests.

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Method for determining colloid size using acid-base titration

(from Mark Jarand, Colloidal Solutions, e-mail of December 12, 2004.)

Procedure, used by Colloidal Solutions for determining surface area of production sols, is based on work by G.W. Sears (1956: Journal of Analytical Chemistry, vol. 28, p. 1981).

Uses 1.5 grams of silica solids as sol, 0.1N NaOH and 0.1 N HCl, 30 grams NaCl

1) In a 300 ml beaker with magnetic stir bar add sol comprising of 1.5 gm silica solids, + water to 135 ml total volume, titrate down to 3.5, note amount of acid used; 0.1N HCl

2) Add 30 gm NaCl; Mix rapidly until dissolved

3) Adjust pH to 4.0

4) Titrate rapidly from pH 4.00 to pH 9.00, end point stable 1 minite plus or minus 0.05 pH.

5) Note mls of 0.1N Base used. ( Vt)

Calculate Surface area; SA (m2/gm) = 26.4(Vt-Vb)

Note. Vb = blank (about 0.3 ml)(titration without silica, but with salt)

Calculate Estimated Average Particle size; P size nm = 3100/SA

Calculate silica to sodium ratio; expressed as gm SiO2/ gm Na20

This is calculated from knowing that the sample contained about 1.5 grams of silica and you can calculate the alkalinity from step 1, amount of acid used. Calculated moles of HCL used, then express as moles Na20, (half of moles of HCl) then grams Na2O.

R (ratio) = 1.5/ gm Na2O

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## 10.6.3 Market testing results

### 10.6.3.1           Byers Rubber Consulting Reports

Sample of geothermal silica precipitates were sent to John Byers of Byers Rubber Consulting for testing.  The geothermal silica was mixed with rubber precursors and cured to form a semitransparent rubber for testing.  Several standard  physical properties tests were performed including Brabender, stress/strain, Zwick rebound, and Pico abrasion tests (see Appendix 13.5).  The first samples that were analyzed did not reinforce the rubber compound very well.  The tensile strength and abrasion loss (Pico abrasion) indicate a reinforcement level in the range of a low surface area silicate or silica.  The very fast cure rate shown in the rheometer data suggests that the pH of sample may have been high (greater than 8).  Our consultant concluded that our precipitation process may be producing 'chunks' of silica with low surface area or with micropores that are too small for polymer chain access, and suggested we perform desorption BET measurements in order to measure pore size.

Test results for silicas produced during later field tests are provided in Appendix 13.5.  Results show that one of the test silicas had favorable properties for silica reinforcement, while all of the others were inferior. These silicas were produced at higher pH values than those tested previously.

Figure 11 shows schematically how silica particles act to reinforce tire rubber and therefore provides guidance for optimizing silica properties for rubber reinforcement. Silica chunks that are held together too strongly would not allow penetration of the polybutadiene chains that is necessary

for good rubber reinforcement.  It is likely possible to produce a less strongly agglomerated silica by lowering the pH and using a shorter residence time. However, these silicas would probably not be captured in our 0.2 micron filters based on tests to date. Use of finer ultrafilters should allow us to adjust processing conditions to produce a silica that makes a better rubber additive.  This work was not followed up on because we changed our targeted silica by-product to colloidal solutions for reasons discussed in section 3.3.3. However, this information will be useful for transferring knowledge from this project to silica extraction efforts at other geothermal sites.
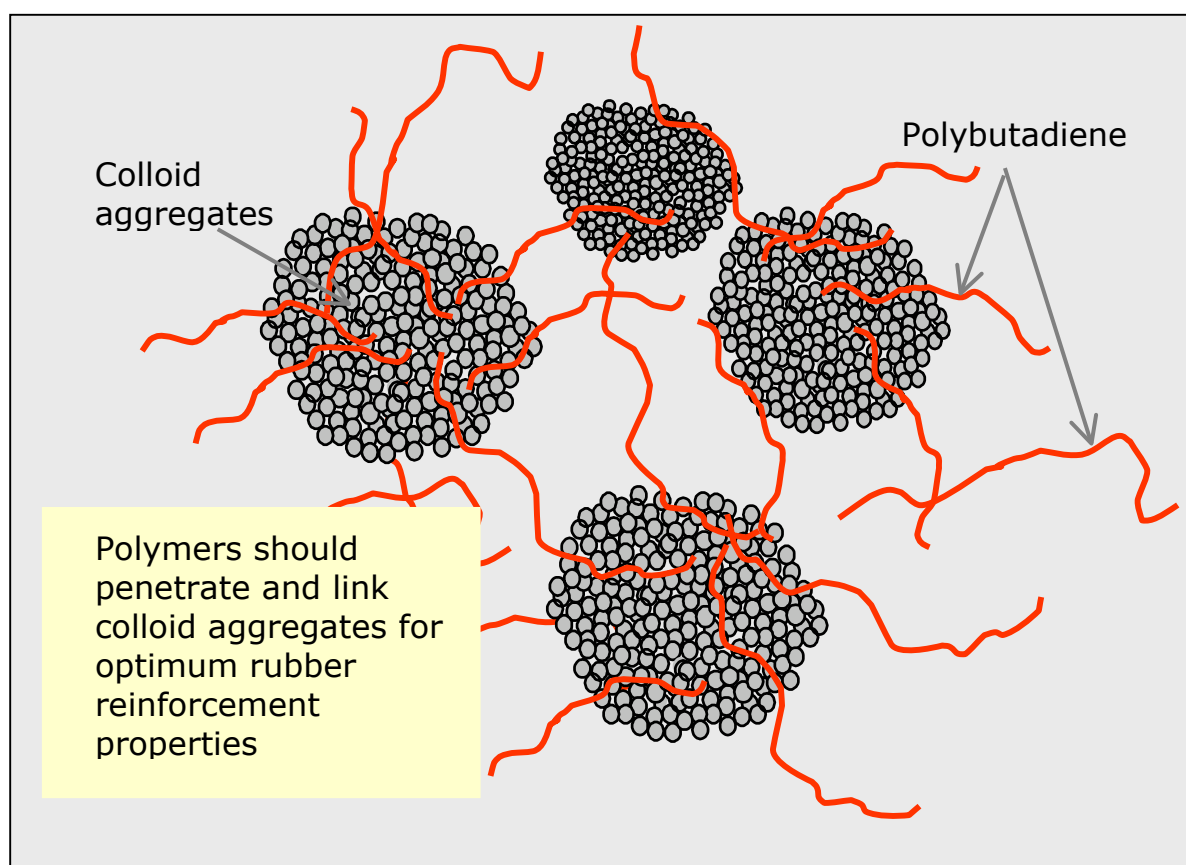


**Figure 11**. Schematic of the mechanism through which silica acts to reinforce the strength properties of tire rubber.  The silica agglomerates should have a pore size that allows polybutadiene polymers to penetrate the silicas and thus allow the polymers to link the silica particles.  The linkage provides favorable physical properties such as resistance to wear abrasion and high tensile strength.

10.6.3.2     Colloidal Solutions reports

Four liters of colloidal silica solutions collected during our December 2004 field work were provided to Mark Jarand of Precision Colloids. Initial attempts to concentrate the solutions to higher than 20 wt % silica were unsuccessful. Work is in progress to finish this work so that market testing can proceed (paid for by Precision Colloids). Related to this, samples have been submitted to Emory University for transmitted electron microscopy (TEM) imaging to determine colloid size and size distribution for our samples.

10.6.4 Preliminary Economic Analysis of Geothermal Silica Marketing

We carried out a preliminary economic analysis of silica extraction for our extraction process.  To do this, we used commercial software designed to estimate costs for water treatment plants.  This method has merit because our extraction process uses standard water treatment methods (reverse osmosis and ultrafiltration) and a stirred reactor that has similarities with equipment used in water softening.  The program is quite thorough and considers costs associated with all of the following: capital equipment including buildings, installation, achitecture and engineering design, operating costs including energy, manpower, membrane cleaning and replacement (including equipment for cleaning), chemicals, disposal costs, and indirect costs for financing, contingencies, and costs for working capital. The program assumes a 20 year plant amortization duration and an interest rate of 8%.

The program WTCOST[6] (Moch, 2002) provided the data used as input to carry out the cash flow calculation shown in Figure 12 below.  These numbers are estimates for extracting silica from 1.5 million gallons per day (MGD) of geothermal fluid, a volume needed to produce enough fluid for the evaporative coolers. The entire geothermal fluid volume currently being produced at Mammoth Lakes  is 18 MGD.  When using this program we were not able to take advantage of the fact that the fluid will be treated at elevated temperatures, which is favorable for both RO and ultrafiltration in that it allows a much greater flux per unit area of membrane as compared to ambient conditions, because of the 50% decrease in water viscosity in going from 25 to 60$^{\circ}$C.  Capital costs for RO and UF elements would therefore be lower than we have indicated.

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[6] I. Moch & Associates, April 2002, "WTCOST: A Water Treatment Cost Estimation Program", Available from the U. S. Bur of Reclamation, Technical Communications Group, Technical Service Center, Denver, Colorado.

Our results suggest the investment would have a positive impact on power plant economics, with a 14% rate of return and payout in 7 years. For comparison, Caithness Operating Company reports extraction and sale of silica would result in a 20% reduction in geothermal power costs at the Dixie Valley geothermal power plant in Nevada.

Note that economics could be made even more favorable by extraction of several other marketable by-products, in addition to silica. The 1.5 MGD stream proposed for processing for silica also contains $121,000 worth of lithium, $210,000 worth of tungsten, and several million dollars worth of cesium and rubidium on an annual basis. There is currently insufficient world market for the amounts of cesium and rubidium present in the Mammoth fluids.
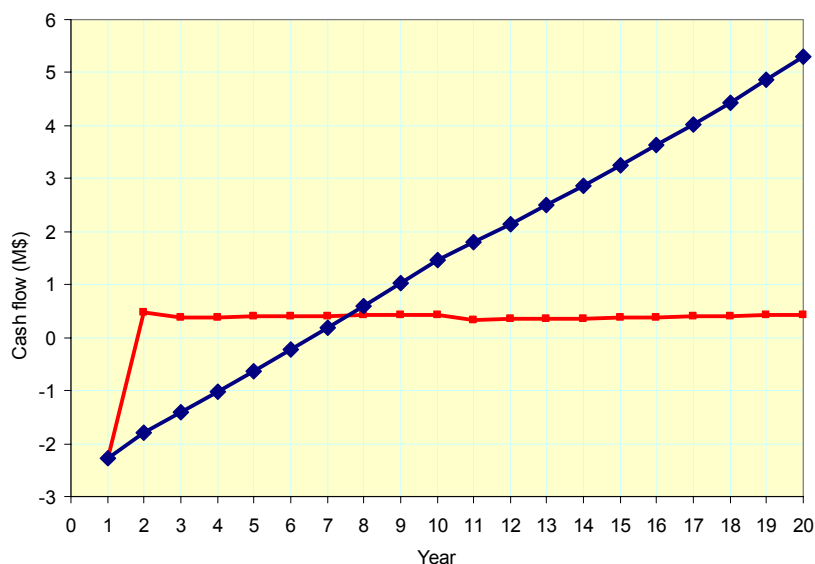


**Figure 12**. Cash flow diagram for silica extraction from 1.5 MGD stream of geothermal fluid. Process provides 1.1 MGD of permeate for evaporative coolers and 0.4 MGD of concentrate for silica extraction.

## 11 Conclusions and Recommendations

11.1 <u>Conclusions</u>

We have shown that we can produce marketable silica by-products, both as a solid precipitate useful in rubber binder applications, and a colloidal slurry useful in precision casting and paper applications.  The market value of silica that could potentially be produced from the Mammoth Lakes site if the entire fluid stream is used for silica extraction is about $11,000,000/year based on a typical market price of $0.75/lb. for precipitated silica used in rubber manufacture and a silica recovery of 7200 tons per year[7].  For a process that treats and extracts silica from a volume of fluid stream sufficient only to provide a low-salt fluid for use in evaporative cooling panels (~1.1 mgd), the estimated capital cost for the extraction technology we have identified is about $2,300,000 with operating costs of about $700,000 per year.  The value of silica produced is $900,000. These preliminary estimates suggest a rate of return of 14% and payout in 7 years.

These estimates are highly preliminary, however.  We believe that uncertainty in the economics of silica extraction has been the major impediment to the commercialization of silica co-production.  Pilot testing will be required to optimize the design of a silica extraction system and to validate that design by long-term testing.  Data from the pilot tests can then be used to rigorously determine the economic feasibility of commercial silica extraction at the Mammoth Lakes site.

11.1.1 Workshop on resource extraction from geothermal fluids

A series of workshops on the extraction of resources from geothermal fluids[8] are being organized by the International Geothermal Association and the Russian Geothermal Society. They will be sponsored by the World Bank/Global Environmental Facility, the Kamchatka Scientific Center (Far East Division of the Russian Academy of Science), and the U.S. Department of Energy. Two LLNL staff (Bruton and Bourcier) will serve as technical organizers for this meeting.

The first workshop is to be held in Kamchatka, Russia in September 12-16 of 2005.  A follow-up meeting is planned for a U.S. location in 2006.  John Lund (U.S.), Marcel Rosca (Romania), and Gordon Bloomquist (U.S.) prepared the proposal to the World Bank which was reviewed favorably in September of 2004.

11.1.2 Impact on geothermal industry

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[7]  Projections for marketing colloidal silica yield similar estimates because of similar market prices for solid and colloidal slurry by-products when normalized to grams of silica.
[8]  Web site at http://geoheat.oit.edu/minerals/minerals.htm

Resource extraction from geothermal fluids already has economic viability, and its demand is likely to increase in the future. Caithness reports that at their Dixie Valley site, data from pilot silica extraction tests suggest the cost of producing power will decrease by about 1 cent per kW-hour. As mentioned previously, this reduces the overall power production cost by about 20%, a very significant reduction.

Recall that our preliminary results suggest investment in silica extraction would return about 14% on the investment. Whether capital should be used to build silica extraction equipment, or develop new geothermal fields is a question of how the relative rates of return for the two compare.

Resource extraction from geothermal fluids is likely to become more favorable in the future for several reasons. Mining of resources, the same resources that can be produced from geothermal fields, is a very energy intensive process. Ore must be dug up, crushed, separated and refined. All these processes demand energy and develop waste streams. In the future, a greater price is likely to be paid for energy and for waste stream treatment for mining. In addition, a greenhouse gas tax is likely to be implemented in the U.S. at some point in the near future, as is currently being done in some European countries. This would add to the cost of mining operations. Resource extraction from geothermal fluids will always be much more energy efficient than mining operations because it eliminates the energy-intensive steps of removing and concentrating the resource from an ore or a brine.

In the short term, any reduction in power plant production costs by producing marketable by-products will help geothermal to compete with fossil fuel plants.

In addition, as technologies are developed to extract not only silica, but other resources such as lithium, cesium, rubidium, bromine, iodine, and others, the economics will become more favorable. Resource extraction from geothermal fluids can leverage off current R&D efforts aimed at selective clean-up of contaminated waters. These technologies are able to selectively extract targeted species, such as arsenic or perchlorate, from contaminated fluids using 'smart' membranes. Spin-off technologies to extract resources from oil and gas-field brines are already under development. In the future, we can expect the development of technologies to extract multiple marketable species from one geothermal system. In some cases where the demand is present, the water itself may be a valuable resource once these species have been extracted.

11.1.3 Impact on silica industry

Silica extraction from geothermal fluids will impact the silica industry by providing a lower-cost silica source. However, given the very large size of the current market for precipitated and colloidal silicas (6 million pounds per day for precipitated silica) the geothermal impact will not be significant. If all the current geothermal systems extracted all their silica, they would produce about 3 million pounds per day. Although significant, we are many years away from the geothermal silica source being a large fraction of the current silica market. Furthermore, by providing a lower-priced silica product the number of applications for silica will increase and thus the market for these types of products likely will grow.

## 11.2 <u>Technology Transfer</u>

As a result of this project, we have generated new methods for producing marketable silica from fluids. These methods can be applied to other geothermal sites. Specific examples include: (1) a methodology to "tune" extraction conditions to produce a silica with desired physical properties; (2) working method(s) to extract arsenic and other contaminants from precipitated silica; (3) development of improved (low maintenance, high efficiency) silica separation techniques using ultrafiltration. The results will be documented and made available to others through written reports and publications in the peer-reviewed literature.

## 11.2.1 Papers and reports

Bourcier, W.L., Nix, G. and Lin, M.S., 2003. Recovery of Minerals and Metals from Geothermal Fluids, Society of Mining and Metallurgical Engineers. SME Annual Meeting, Cincinnati Ohio.(abstract). Full paper available from Lawrence Livermore National Laboratory Report UCRL-JC-153033.

Bourcier, W.L., Wallace, A., Ralph, B. and Bruton, C., 2002. Silica extraction at the Mammoth, California geothermal site, Geothermal Resource Council Annual Meeting, Reno, Nevada. (poster).

Burton, E. A., W. L. Bourcier, A. Wallace, C. J. Bruton, and R. Leif, 2003. Silica scale management: Lowering operating costs through improved scale control and adding value by extracting marketable by-products. Geothermal Res. Trans. V. 27 (in press).

## 11.3 <u>Recommendations for future work</u>

The results of our December 2004 field session are encouraging and instructive. While we definitely see an increased silica concentration in the ultrafiltered slurry, represented by the qualitative increase in RI and the

quantitative increase in density, comparing our samples to the industry samples indicates that we need to concentrate the silica in solution even further (see Appendix 13.2).

The most important need in order to commercialize silica co-production is to carry out a pilot-scale project where the data on the silica recovery rates, membrane lifetimes and cleaning needs, silica homogeneity, and other process parameters can be measured over week to month long performance intervals. These data are key for carrying out a detailed economic analysis of full-scale production.

## 11.4 Other geothermal sites with favorable characteristics for silica extraction

Mammoth Lakes is an ideal site to attempt silica extraction both because of the high purity of the fluids, which makes a high purity silica by-product possible without extensive cleaning, and because of the dual use of the process to both provide silica-depleted fluid for cooling applications, and silica enriched fluid for silica extraction.

In the future, other binary geothermal plants can take advantage of the silica extraction technology developed at Mammoth Lakes (Table 4). All such sites have a need for pure water for cooling towers, and can benefit from the marketable by-product. Most binary plants (several of which are located in Nevada and owned by Ormat, the company that owns 50% interest in the Mammoth Lakes plant) utilize a relatively low-temperature source fluid that tends to have low salinity levels that are slightly higher than, but comparable to, Mammoth Lakes. Flash plants, on the other hand, generally operate using a higher temperature fluid but the fluids also generally have higher salinities.

Although reverse osmosis is used at Mammoth Lakes to generate a concentrate for silica extraction, in doing so the process generates a fluid that is quite similar to geothermal fluids at other sites.  Table 5 and Figure 13 compare California, Nevada, and Utah geothermal systems in terms of fluid salinity and silica content, two key parameters that affect the silica extraction process. Note that the reverse osmosis "processed" fluids that are used for silica extraction are fairly similar in composition to fluids from other geothermal systems, in particular Medicine Lake Highlands and Dixie Valley. Also, many fluids used at Coso are only slightly higher in salinity than the corresponding Mammoth Lake concentrate.

**Table 4**. Processing steps for producing silica at Mammoth Lakes and their applicability to other geothermal systems.

| Processing Step | Unique to Mammoth Lakes | Applicable with some modification | Generally applicable |
|---|---|---|---|
| Reverse Osmosis | ✓ | | |
| Precipitation method | | ✓ | |
| Filtration method | | | ✓ |
| Post-processing | | | ✓ |
| Characterization | | | ✓ |
| Removal of impurities | | ✓ | |
| Market testing | | | ✓ |

**Table 5**. Comparison of silica concentration, salinity, and pH of fluids from geothermal systems fluids in the Western U.S.

| | Silica (ppm) | Salinity (ppm) | pH | Production Method |
|---|---|---|---|---|
| ML Raw | 250 | 1600 | 6.8 | Binary |
| ML RO # 1 | 750 | 4800 | 7.2 | Binary |
| ML RO # 2 | 1000 | 6400 | 7.3 | Binary |
| East Mesa | 165 | 6470 | 6.1 | Flash |
| Heber | 294 | 14200 | 6.5 | Binary |
| Coso # 1 | 382 | 4800 | 7.9 | Flash |
| Coso # 2 | 1020 | 9780 | 6.2 | Flash |
| Coso # 3 | 730 | 7050 | 8.0 | Flash |
| Dixie Valley | 490 | 1650 | 9.0 | Flash |
| MLH | 442 | 2340 | 8.5 | (und.)[*] |
| RHS | 631 | 8320 | 8.1 | Flash |

ML Raw = Untreated Mammoth Lakes geothermal fluid
ML RO #1 = Mammoth Lakes fluid, reverse osmosis concentrate
ML RO #2 = Mammoth Lakes fluid, reverse osmosis concentrate with recycle
East Mesa = East Mesa and Heber data from EPA Report /816-R-99-014q
        "Class V Underground Injection Control Study" 1999.
Coso # 1 = Well 16-8 (Bishop and Bird, 1987; Geoch. Cosm. Acta. 51:1245.
Coso # 2 = Sample from East Flank plant  (Ted De Rocher, pers. com.)
Coso # 3 = Sample from "Navy # 1" well (Ted De Rocher, pers. com.)

Dixie Valley = Dixie Valley, NV from Bruton et al, 2002 (GRC 21, p. 157-164) flash corrected

MLH = Medicine Lake Highlands, Sample from Telephone Flat well 87-13, http://www.ca.blm.gov/alturas/telephone/

RHS = Roosevelt Hot Springs, 2001, Pers. com. Bill Lewis, Power Engineers

* und: this site has not been fully developed at this time.
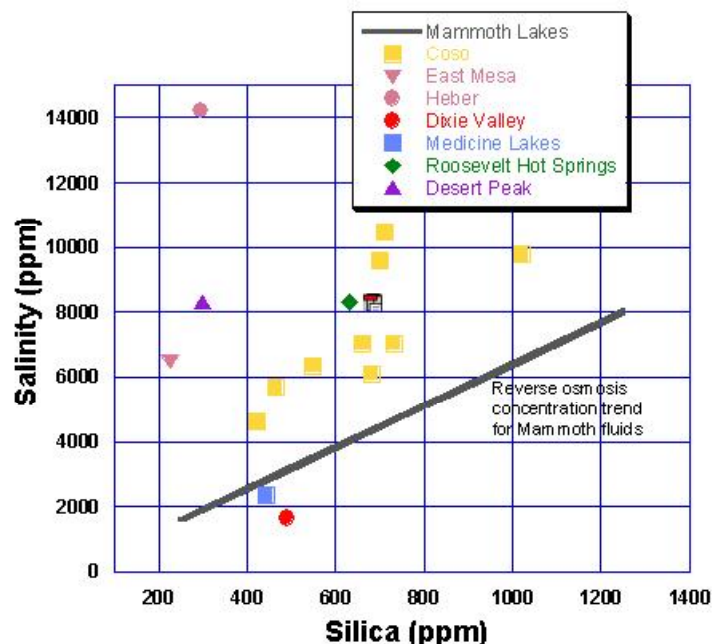


**Figure 13**. Plot of salinity vs. silica concentration of Western U. S. geothermal systems. Line shows composition of reverse osmosis concentrate generated from Mammoth Lakes fluid. Note the similarity of processed Mammoth fluids to other systems such as Coso, Medicine Lake, and Dixie Valley.

## 12  Project Management Information

### 12.1  Budget history

The rate of spending on this project is shown in Figure 14. A quarterly breakdown is provided in Table 6. Also, a comparison of the funds provided by the Energy Commission and the Department of Energy is given in Table 7. Note that our cost share funding is provided by DOE from two sources; Geothermal Technologies and Forest Products of the Future.
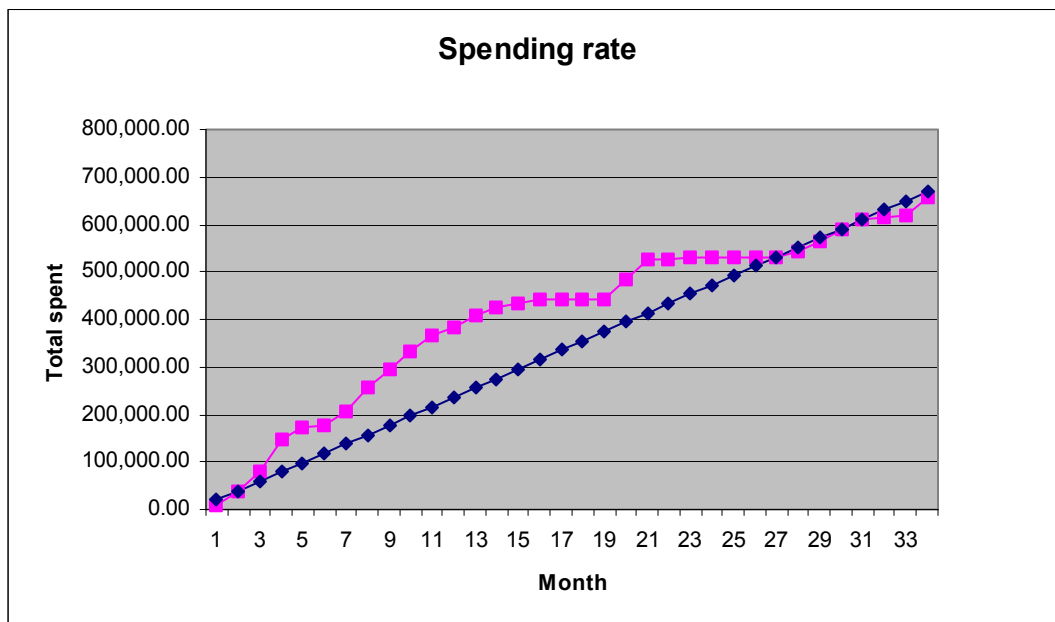
**Figure 14**. Cumulative spending vs. flat spending over project duration.

**Table 6**.  Allocation of California Energy Commission funds from 2002-2004.

| | | Labor | Subcontracts | Travel | Supplies | Overhead | **Spending/Quarter** |
|---|---|---|---|---|---|---|---|
| Original Budget | | $204,745.00 | $48,819.00 | $15,188.00 | $33,552.00 | $367,379.00 | $669,683.00 |
| 1st Quarter | Mar - Jun 02 | 58,645.84 | - | 1,974.27 | 10,137.59 | 87,793.28 | 158550.98 |
| 2nd Quarter | Jul - Sep 02 | 19,316.74 | - | - | 14,848.50 | 29,540.48 | 63705.72 |
| 3rd Quarter | Oct - Dec 02 | 49,353.22 | - | 3,326.03 | 9,757.89 | 64,941.41 | 127378.55 |
| 4th Quarter | Jan - Mar 03 | 29,035.76 | 2,312.00 | 1,659.16 | 4,152.65 | 38,644.38 | 75803.95 |
| 5th Quarter | Apr - Jun 03 | 10,536.05 | 795.00 | - | 4,440.27 | 17,329.43 | 33100.75 |
| 6th Quarter | Jul - Sep 03 | 5,412.34 | (133.95) | - | 1,893.22 | 5,816.28 | 12987.89 |
| 7th Quarter | Oct - Dec 03 | 31,653.86 | 3,300.00 | 17.50 | 8,756.86 | 39,104.33 | 82832.55 |
| 8th Quarter | Jan - Mar 04 | (107.25) | 1,180.08 | - | 242.22 | 1,172.53 | 2487.57 |
| 9th Quarter | Apr - Jun 04 | 5,086.94 | 0 | | 1144.83 | 5943.81 | 12,175.58 |

| 10th Quarter | Jul - Sep 04 | 25,455.24 | 0 | 315.35 | 14,697.33 | 27687.18 | 68,155.10 |
| 11th Quarter | Oct - Dec 04 | 14,827.78 | 0 | | 1938.85 | 16,117.91 | 32,884.54 |

NB:  No equipment was purchased using California Energy Commission funds.
        (Any necessary equipment was purchased using DOE matching funds.)

**Table 7**. Project budget totals

| Calendar Year | CEC Funding ($K) | DOE Cost Share ($K) | Total |
| --- | --- | --- | --- |
| 2002 | 350 | 100 | 400 |
| 2003 | 205 | 80 | 350 |
| 2004 | 115 | 20 | 120 |

## 13  Appendices

### 13.1  Appendix - Silica extraction from simulated Mammoth Lakes geothermal fluids in laboratory tests

Preparation of Synthetic Brine

The Geochemist's Workbench[9] software was used to create a synthetic brine solution with the same composition as the geothermal fluid at Mammoth Pacific LP.  For the purpose of maintaining the stability of species in solution, the synthetic brine was prepared as two separate solutions:  one solution contained sodium silicate only, and was prepared at pH 11 - 12 in order to ensure that the silica stayed in solution without polymerizing; the other solution was a concentrated salt mixture, which was prepared at pH 2 – 3 to prevent precipitation of the dissolved brine constituents as carbonate phases.  The brine itself was synthesized by mixing the sodium silicate solution and the salt solution in the appropriate proportions prior to the start of each experimental run.  The composition of the synthetic brine, and the Mammoth Pacific LP brine are shown below in Table A13.1-1.

**Table A13.1-1**.  Table showing the composition of the Mammoth Pacific LP geothermal brine in comparison to the composition of the synthetic brine.

| Species | Mammoth Pacific LP Composition (09/22/1997) Concentration (ppm) | Simulated Brine Composition Concentration (ppm) |
|---------|--------------------------------|--------------------------------|
| Na | 351.76 | 351.43 |
| K | 31.84 | 31.50 |
| Ca | 2.05 | 2.05 |
| Fe | 0.15 | - |
| B | 10.5 | - |
| Li | 2.04 | 2.05 |
| Sr | 0.12 | - |
| As | 1.47 | - |
| $NH_4$ | 0.43 | - |
| $HCO_3$ | 400 | 399.90 |
| Cl | 239 | 309.80 |
| F | 11.39 | - |
| $SO_4$ | 110 | 109.70 |
| S | 6.9 | - |
| $SiO_2$ | 254.46 | 254.00 |

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[9] Bethke, C. (1998) Geochemists Workbench Geochemical Modeling software. Available from Rockware, Golden, Colorado. http://www.rockware.com/

The concentrations of the major species in the synthetic brine accurately mirror the concentrations of the major species in the Mammoth Pacific LP brine. The slightly inflated Cl concentration is caused by the adjustment of the concentrated salt solution to pH 2-3 with HCl. Some minor elements were omitted from the synthetic brine recipe but should not significantly affect the outcome of the laboratory experiments.

Preparation of the Sodium Silicate Stock Solution

A concentrated sodium silicate solution (~10, 000 ppm as $SiO_2$) was prepared by dissolving 10 g / L Cab-o-Sil fumed silica in 0.33 mol / L NaOH. The Cab-o-sil fumed silica does not dissolve readily, and the solution must be heated for 30 – 45 minutes at $40^\circ$ C to fully dissolve the silica; however, once the silica has dissolved, the solution is stable at room temperature. For one liter of 10,000 ppm $SiO_2$ solution, the procedure is as follows:

1) Weigh 10.0 grams of Cab-o-sil fumed silica and place in a 1 L volumetric flask.

2) Add 33 ml of 10 mol/L NaOH to the 1 L volumetric flask.

3) Place a stir bar in the flask, and fill the flask with filtered deionized water to just below the 1 L line.

4) Place a rubber stopper and a thermometer in the flask as shown



**Figure A13.1-1**. Schematic diagram of the apparatus used to make concentrated sodium silicate solutions.
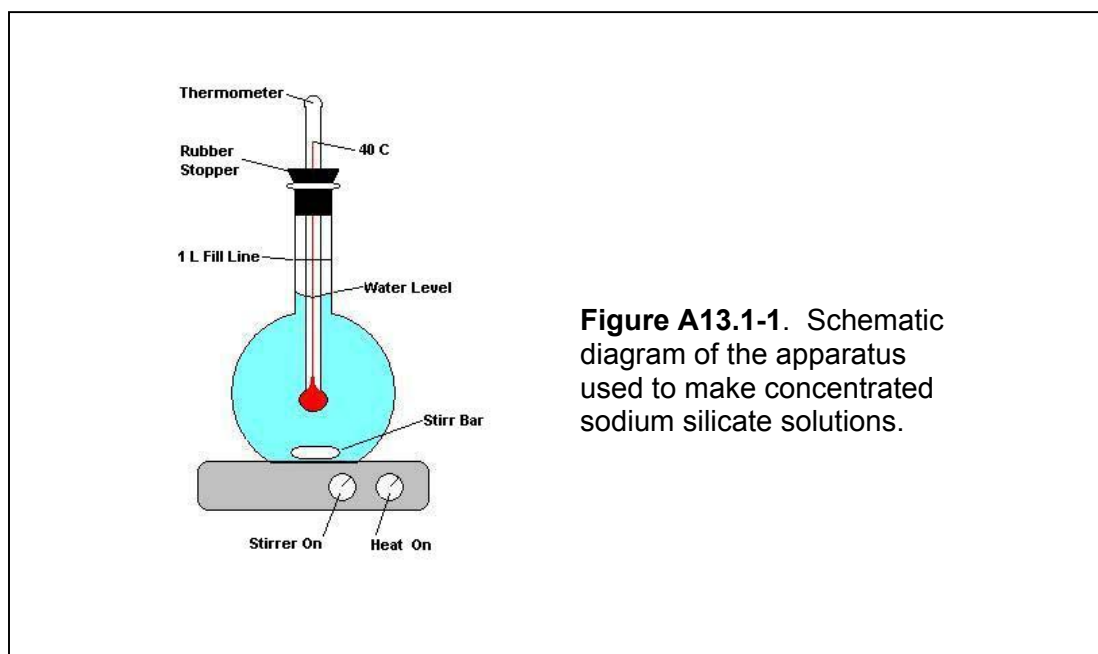
5) Gently stir, and heat the solution to 40° C for 30 to 45 minutes until the solution becomes clear.

6) Let cool and remove the thermometer and stir bar. Fill flask with deionized water to the 1 L line.

7) Mix thoroughly.

The sodium silicate solution has a pH of ~12 and is stable at room temperature. After the sodium silicate solution has been prepared the exact concentration of monomeric silicon in the solution is determined by the beta silicomolybdate method, as described by Iler[10]. The beta silicomolybdate method will be described in detail in the methods of analysis section.


Preparation of the Concentrated Salt Solution

The salt solution was prepared separately from the sodium silicate solution because it had to be kept at pH 2 - 3 order to prevent precipitation of the brine constituents as carbonate minerals. The salt solution was prepared at two times the concentration of the actual brine to prevent unnecessary dilution of the brine during the addition of the sodium silicate solution. For 1 L of doubly concentrated salt solution, the procedure is as follows:

1) Place 500 mL of filtered deionized water in a 1 L graduated cylinder.

2) Place a stir bar in the graduated cylinder and stir vigorously.

3) Add the appropriate number of moles for each salt listed in Table A13.1-2.

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[10] Iler, 1979, The Chemistry of Silica, Wiley Interscience, p. 94-100.

**Table A13.1-2**. Table showing the amount of various salts needed to make 1 L of doubly-concentrated salt solution.

| Salt Added | Moles Added / L |
|:---:|:---:|
| LiCl | 5.90E-04 |
| $H_2SO_4$ | 2.18E-03 |
| KCl | 1.61E-03 |
| $NaHCO_3$ | 1.31E-02 |
| $CaSO_4$ | 1.02E-04 |
| NaCl | 5.13E-04 |
| HCl | 1.48E-02 |

4) Continue stirring until all additives have been dissolved.

5) Remove the stir bar and pour the salt solution into a closed container.

6) With the graduated cylinder measure out 500 ml of filtered deionized water and add it to the salt solution.

The concentrated salt solution has a pH between 2 and 3, and is stable at room temperature.


Experimental Procedure

At the start of each experiment, 200 ml of synthetic brine solution was prepared by mixing 100 ml of concentrated brine solution with 5.08 ml of sodium silicate solution and 94.92 ml of filtered deionized water in an Erlenmeyer flask. The brine was heated to 60° C on a hot plate and the pH was adjusted to ~ 7.00 with hydrochloric acid. The mixture was then treated with $MgCl_2$, $FeCl_3$, or $Al_2(SO_4)_3$ to induce silica precipitation. The effects of cooling and seeding on silica precipitation were also investigated. Samples were taken periodically during each experiment for particle size analysis by DLS, monomeric Si analysis by the beta silicomolybdate method, and total Si by ICP-MS; the experiments typically lasted four hours.

The following procedures were used for the silica yield experiments:

*Experiments at 60$^o$ C*

1) Mix 100 ml of concentrated brine solution, 5.08 ml of sodium silicate solution (10,000 ppm as $SiO_2$), and 94.92 ml of filtered deionized water in an Erlenmeyer flask.

2) Gently heat the solution on a hot plate to 60$^o$ C and stir gently.

3) Adjust the pH to ~ 7.00 with hydrochloric acid.

4) Add the desired amount of silica seeds, $MgCl_2$, $FeCl_3$, or $Al_2(SO_4)_3$ (Usually 20 or 50 mmol / L).

5) Take a 20 ml sample for DLS and monomeric Si as soon as possible. Adjust the pH of the sample to ~ 2.0 with HCl.

6) Take a 20 ml sample for ICP-MS as soon as possible. Filter the sample through a 20 nm Whatman Anatop 25 syringe filter to remove precipitated silica. Adjust the pH of the sample to ~ 11.0.

7) Maintain the brine at 60$^o$ C and continue stirring. Take additional samples for DLS / Monomeric Si, and ICP-MS at 0.5, 1, 2, and 4 hours.

*Cooling Experiments*

1) Prepare the brine as described above in steps 1 – 4.

2) Take a 20 ml sample for DLS and monomeric Si At 60$^o$ C. Adjust the pH of the sample to ~ 2.0 with HCl.

3) Take a 20 ml sample for ICP-MS at 60$^o$ C. Filter the sample through a 20 nm Whatman Anatop 25 syringe filter to remove precipitated silica. Adjust the pH of the sample to ~ 11.0.

4) Rapidly cool the brine to the desired temperature in an ice water bath.

5) Maintain the brine at constant temperature and continue stirring. Take additional samples for DLS / Monomeric Si, and ICP-MS at 0.5, 1, 2, and 4 hours.

Methods of Si Analysis

*The Beta Silicomolybdate Method*

In the presence of the silicon monomer $Si(OH)_4$ molybdic acid reacts to form yellow silicomolybdic acid by the following reaction:

$$7\ Si(OH)_4 + 12\ H_6Mo_7O_{24} \bullet 4H_2O + 174\ H_2O = 7\ H_8Si(Mo_2O_7)_6 \bullet 28H_2O$$
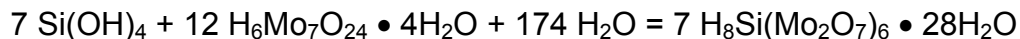
Yellow silicomolybdic acid solutions become more intensely colored as the concentration of monomeric silicon increases; consequently, changes in the light absorbency of silicomolybdic acid solutions are correlated to the concentration of monomeric silicon in solution.

A photospectrometer was used to measure the light absorbency of several silicomolybdic acid solutions of known concentration; all of the solutions were between 0 and 1000 ppm as $SiO_2$ and were prepared with VWR brand sodium silicate solution (1 mg = 1 ml $SiO_2$) and dilute molybdic acid. The light absorbency of each solution (measured at 410 nm) was plotted against the concentration of monomeric silicon in solution. The equation of the linear regression line was used to determine the monomeric silicon concentration of unknown solutions.

The following procedure for the preparation and use of dilute molybdic acid in monomeric Si analyses may be found in Iler, 1979.

*Preparation of Dilute Molybdic Acid*

1) Prepare a 1.5 N sulfuric acid solution. Add 41.0 ml of 95.5% $H_2SO_4$ to 800 ml of filtered deionized water and dilute to 1 L.

2) Prepare an ammonium molybdate solution in the following manner. Dissolve 100 g of $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$ in 900 ml of filtered deionized water. Add 47.0 ml of 28% $NH_4OH$. Dilute to 1 L.

3) To 500 ml of filtered deionized water, add 200 ml of sulfuric acid solution and 100 ml of ammonium molybdate solution. The resulting molybdic acid solution has a pH of ~1.2 and is stable for about one week.

*Calibration of the Photospectrometer*

1) Fill eleven 50 ml volumetric flasks with 40 ml of dilute molybdic acid solution. Label one flask as "blank" and number the remaining flasks from one to ten.

2)  Fill two cuvettes with water.  Measure the absorbency of each water sample, and make sure that the values are the same.  Label one cuvette "blank" and the other "sample."

3)  The molybdic acid solution is nearly colorless but does absorb some light.  To eliminate this effect, fill the "blank" 50 ml flask to the fill line with filtered deionized water and mix thoroughly.  Pour some of the "blank" solution into the "blank" cuvette and insert into the photospectrometer.  Use the dial to zero the absorbency reading.  This procedure will eliminate the background absorbency of the molybdic acid solution.

4)  Add VWR sodium silicate standard solution (1 ml = 1 mg $SiO_2$) to flasks 1-10 in 0.1 g increments from 0.1 g to 1.0 g.  Record the exact weight of solution added, dilute each flask to the fill line and mix thoroughly.

5)  Measure and record the absorbency of the silicomolybdic acid solutions in flasks 1 through ten.  Fill and empty the "sample" cuvette with sample twice before analysis.  This will ensure that the sample in the cuvette has not been contaminated by the previous sample.  Fill the cuvette a third time, insert into the photospectrometer and record the absorbency value.

6)  Create a plot of $\mu$g $SiO_2$ / 50 ml versus absorbency and add a linear regression line (Figure A13.4-2).
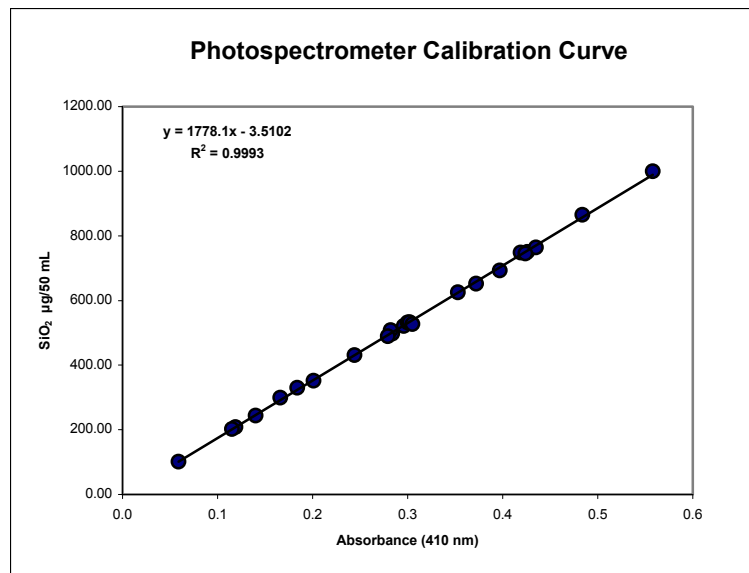
**Figure A13.1-2**.  Photospectrometer calibration plot showing the relationship between monomeric silicon concentration and absorbency.

*Analysis of an Unknown Solution*

The following procedure was used to determine the monomeric silicon concentration of our unknown solutions.

1) Prepare a blank solution by placing 40 ml of dilute molybdic acid solution in a 50 ml volumetric flask.  Dilute to 50 ml with filtered deionized water.  Use the blank solution to zero the absorbency reading on the photospectrometer.

2) Prepare a silica standard solution.  Again, place 40 ml of dilute molybdic acid solution in a 50 ml volumetric flask.  Add between 0.1 and 1.0 g of VWR sodium silicate standard solution (1 ml = 1 mg $SiO_2$).  Record the exact weight of sodium silicate solution added and measure the absorbency.  Add this data to the photospectrometer calibration curve.  If the standard solution plots on or near the regression line, the photospectrometer is working correctly, and the molybdic acid solution has not lost its potency.

3) To analyze the unknown, place 40 ml of dilute molybdic acid solution in a 50 ml volumetric flask.  Add approximately 1.0 g of unknown solution.  Record the exact weight of sample added.  Fill to the 50 ml mark with filtered deionized water, and mix thoroughly.

4)       Measure the absorbency of the unknown solution and use the equation from the photospectrometer calibration curve to determine the concentration of monomeric Si in solution.

## Laboratory and Field Results

### Laboratory Results

Figure A13.1-3 (below) is a graph of monomeric Si versus elapsed time constructed for untreated synthetic Mammoth geothermal brine at pH 7.0 and $60^{\circ}$ C. The data shows that Si is slow to polymerize in a fluid composition similar to the Mammoth geothermal brine. Slight upward trend is probably due to evaporation of water.



**Mammoth Polymerization**
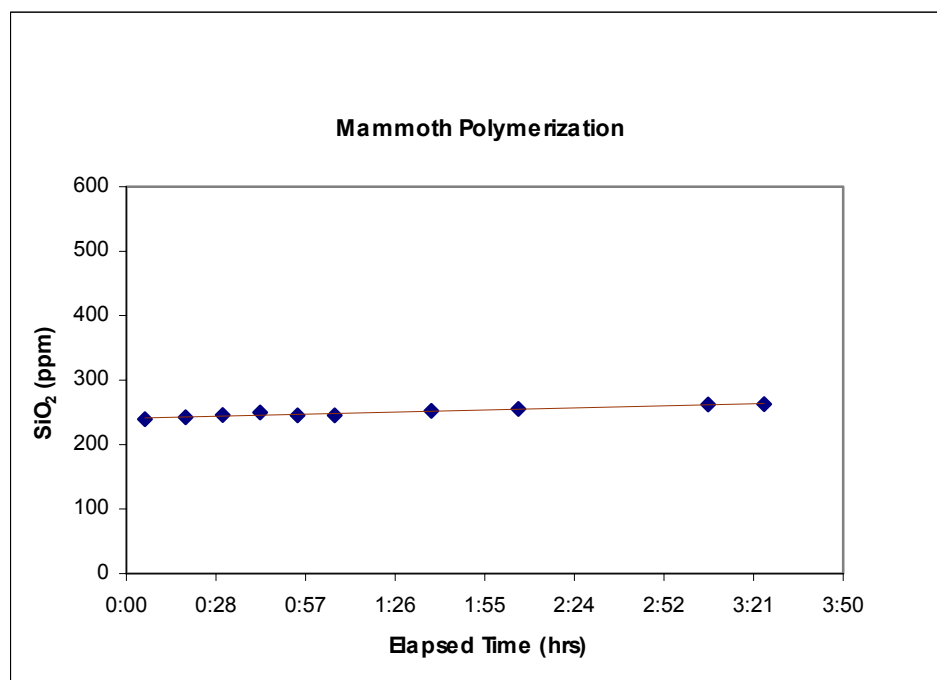
**Figure A13.1-3**. Plot of silica polymerization versus time for Mammoth synthetic brine at pH 7 and $60^{\circ}$C. Y-axis gives monomeric silica concentration which would be decreasing if silica polymerization were taking place.

During our laboratory work we treated the synthetic brine with magnesium chloride, aluminum sulfate, and ferric chloride salts in order to induce silica precipitation. We also experimented with cooling, seeding and pH adjustment. The results of these experiments are shown below in Table A13.1-3.

Most of the experiments failed to produce a silica precipitate (Figures A13.1-4 and A13.1-5).  Even seeded runs failed to show significant particle growth in a short period of time (see Figure A13.1-4).

**Table A13.1-3**.  Table showing the composition of the Mammoth Pacific LP geothermal brine in comparison to the composition of the synthetic brine.

| Sample | SiO2 Concentration (ppm) | Additive | Additive Concentration (mmol / L) | Target pH | Initial pH | pH After Treatment | Cooled Run | Notes |
|---|---|---|---|---|---|---|---|---|
| 032202 (00 - 11) | 254 ppm | MgCl$_2$ | 20 | 7 | 7.06 | 6.83 | no | No Precipitate |
| 032202 (13 - 22) | 254 ppm | MgCl$_2$ | 50 | 7 | 7.04 | 6.71 | no | No Precipitate |
| 032602 (00 - 05) | 254 ppm | - | - | 6 | 5.94 | NA | 0˚C | No Precipitate |
| 032602 (06 - 11) | 254 ppm | - | - | 7 | 7.02 | NA | 0˚C | No Precipitate |
| 032702 (00 - 05) | 254 ppm | - | - | 8 | 8.05 | NA | 0˚C | No Precipitate |
| 032702 (06 - 11) | 254 ppm | MgCl$_2$ | 20 | 7 | 7 | 6.71 | 0˚C | No Precipitate |
| 032802 (00 - 05) | 254 ppm | MgCl$_2$ | 20 | 6 | 5.66 | 5.53 | 0˚C | No Precipitate |
| 032802 (06 - 11) | 254 ppm | MgCl$_2$ | 20 | 8 | 8 | 7.75 | 0˚C | No Precipitate |
| 032902 (00 - 05) | 254 ppm | MgCl$_2$ | 50 | 6 | 6.04 | 5.62 | 0˚C | No Precipitate |
| 032902 (06 - 11) | 254 ppm | MgCl$_2$ | 50 | 7 | 6.98 | 6.6 | 0˚C | No Precipitate |
| 040302 (00 - 09) | 600 ppm | - | - | 7 | 7 | 7 | 25˚ C | No Precipitate |
| 040402 (00 - | 254 ppm | MgCl$_2$ | 20 | 9.5 | 9.55 | 8.14 | no | No Precipitate |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 09) | | | | | | | | |
| 041202 (00 - 09) | 254 ppm | $MgCl_2$ | 20 | 9.5 | 9.54 | 8.23 | 0°C | No Precipitate |
| 41602 | 254 ppm | $FeCl_3$ | 20 | 9.5 | 9.51 | ~ 1.5 | no | Experiment stopped; raised pH with NaOH and formed deep red precipitate |
| 042202 (00 - 09) | 254 ppm | $FeCl_3$ | 2.2 | 7 | - | 6.29 | no | Brown Precipitate |
| 042302 (00 - 09) | 254 ppm | $FeCl_3$ | 20 | 9.5 | - | 9.12 | no | Brown Precipitate |
| 042602 (00-09) | 254 ppm | $Al_2(SO_4)_3$ | 4 | 9.5 | - | 8.8 | no | Precipitate dissolved at low and high pH |
| 042902 (00-09) | 254 ppm | $Al_2(SO_4)3$ | 10 | 9.5 | - | 9.01 | no | Precipitate dissolved at low and high pH |
| 050102 (00-09) | 254 ppm | Cab-O-Sil Silica | 50 mg / L | 9.5 | 9.52 | 9.51 | 25° C | - |
| 050202 (00-12) | 254 ppm | Cab-O-Sil Silica | 130 mg / L | 7 | 7.25 | 7.25 | 25° C | Monomeric Si analysis showed little to no particle growth. |
| 050702 (00-11) | 600 ppm | - | - | 7 | 6.74 | 6.74 | 25° C | - |
| 051302 (00-11) | 500 ppm | - | - | 7 | 6.93 | 6.93 | 25° C | - |
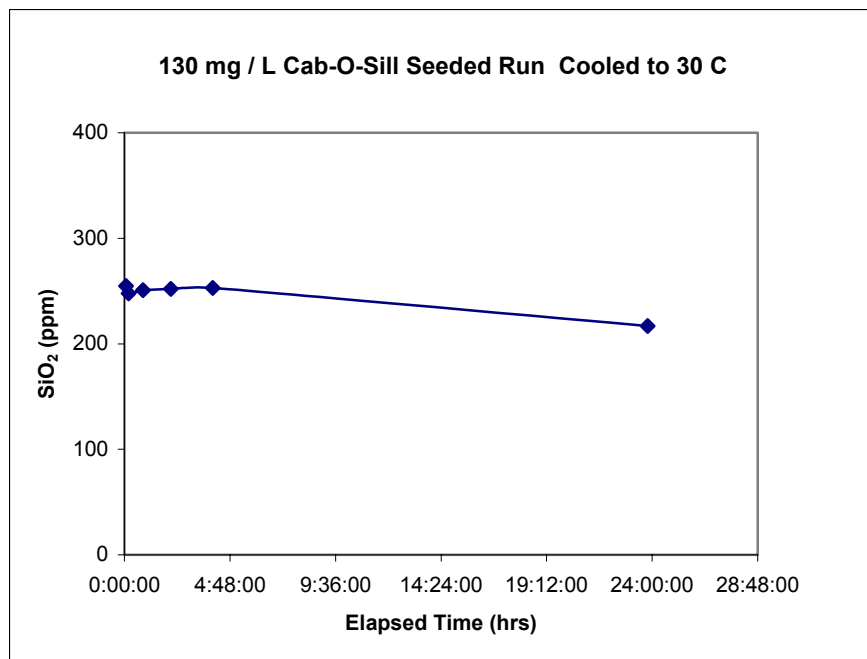
**Figure A13.1-4**.  Plot of monomeric silica vs. time showing the slow polymerization of silica in the presence of silica seeds over a 24-hour period.
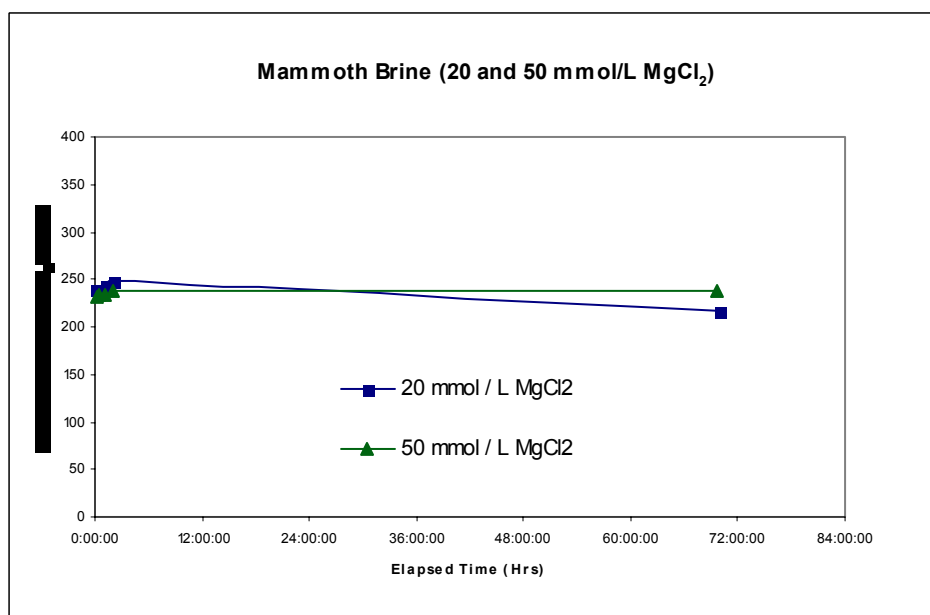


**Figure A13.1-5**.  Plot showing the slow polymerization of silica in the presence of 20 mmol / L and 50 mmol / L magnesium chloride over a 72-hour period.

 A set of runs at pH 9.5 with 20 mmol / L magnesium chloride showed no evidence of a silica precipitate.  Three weeks later, however, a thin silica gel was found on the bottom of the sample container.  The monomeric Si analysis shown below in Figure A13.1-6 was performed after the film was discovered.
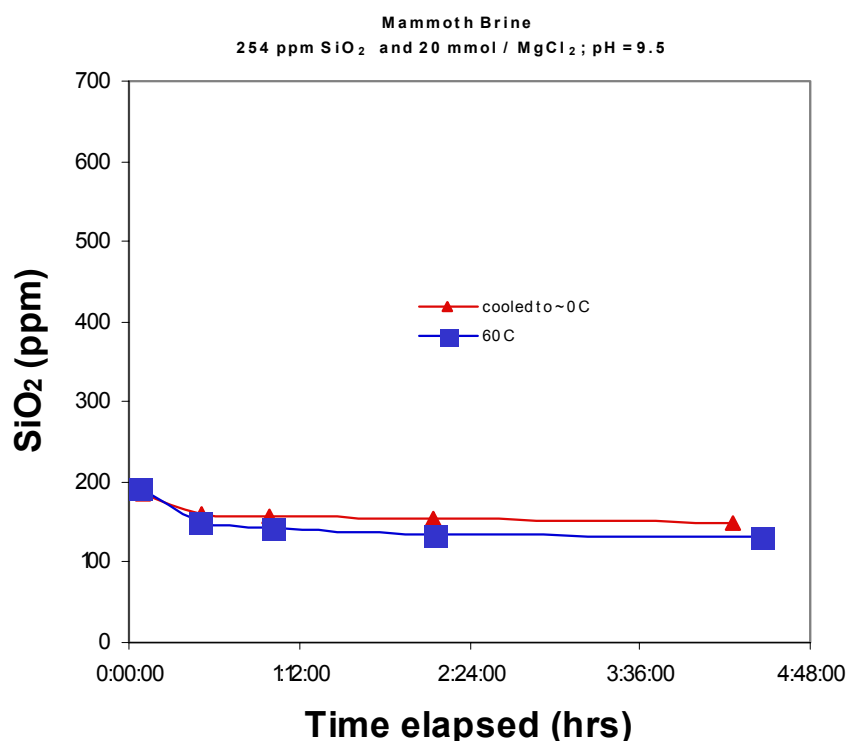


**Figure A13.1-6**.  Monomeric silica versus elapsed time at pH 9.5 with 20 mmol/ L magnesium chloride added.  Decrease in monomeric silica indicates amount of silica polymerization. Data represented by the triangular series was collected at 0°C;  data represented by the square series was collected at 60°C.

The Mammoth geothermal brine contains ~254 ppm silica.  However, it may be possible to concentrate silica in solution by reverse osmosis filtration or by evaporation.  We completed two experiments at elevated silica concentrations (Figure A13.1-7); the rate of silica polymerization was much more rapid in the 500 and 600 ppm silica brine than the 254 ppm brine.
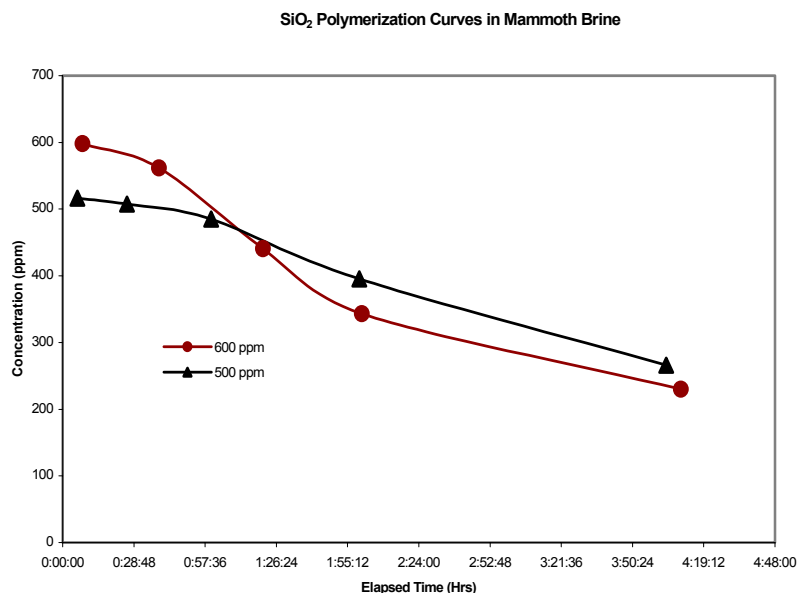
**Figure A13.1-7**. Monomeric silica vs. time. Decrease in monomeric silica indicates substantial amount of polymerization of silica in Mammoth synthetic brine at elevated silica concentrations. These data suggest concentrating silica using reverse osmosis will be an effective way to produce a silica by-product in a reduced amount of time.
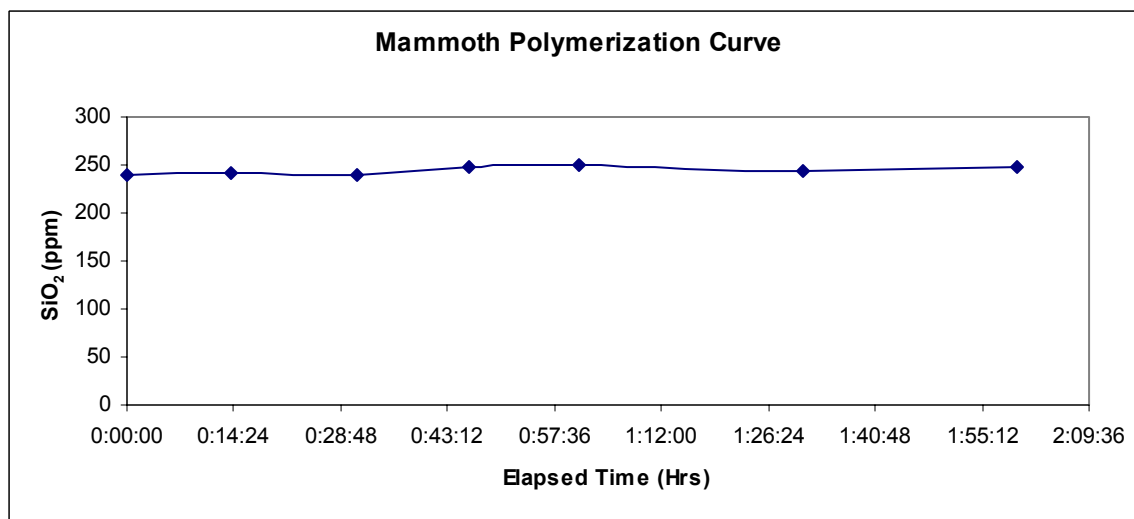


**Figure A13.1.8**. Plot showing the stability of silica in solution over a two hour period.

*Field Results*

Figures A13.1-8 and -9 (below) are plots of monomeric silica versus elapsed time constructed for untreated Mammoth Pacific LP geothermal brine at pH ~ 7.0. The data shows that Si is just as slow to polymerize in

the geothermal fluid as it is in the synthetic brine solution.  These observations are consistent with theoretical models of low silica systems.
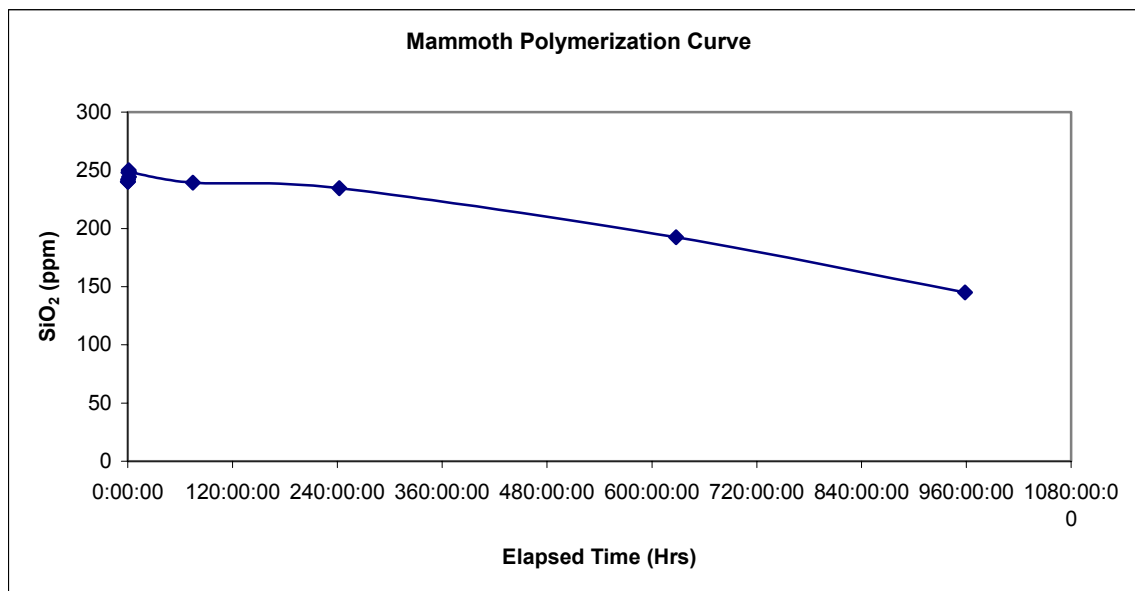


**Figure A13.1-9**.  Plot showing the polymerization of silica in Mammoth geothermal fluid over a 40-day period.

The experiments conducted in the field were very similar to those in the laboratory.  We introduced magnesium chloride and aluminum sulfate salt solutions to the brine in order to induce silica precipitation.  The salt solutions were pumped at a constant rate into a 20 L reactor full of flowing brine.  After a few minutes the contents of the reactor reached a steady state, and samples were taken for particle size analysis by DLS, monomeric Si analysis by the beta silicomolybdate method, and total Si analysis by ICP-MS.  Monomeric Si analyses were conducted in the field for the samples listed in Table A13.4-4.  The monomeric Si as $SiO_2$ for all the samples is very close to the total initial silica content of 254 ppm; the magnesium chloride and aluminum sulfate salt treatments had little effect on the polymerization of Si.

**Table A13.1-4**.  Summary of Field Results

| Table A8.5 3 - Summary of Field Results | | | | | |
|---|---|---|---|---|---|
| Sample | Brine pH | Monomeric Si as $SiO_2$ | Additive | Additive Concentration | Vessel Temperature (C) |
| m-0612a-01 | 6.72 | 222.42 | $MgCl_2$ | 0.33 mol / L | 68.6 |
| m-0612a-03 | 6.65 | 242.20 | $MgCl_2$ | 0.33 mol / L | - |
| m-0612a-05 | 6.67 | 250.12 | $MgCl_2$ | 0.33 mol / L | 65.8 |
| *m-0613a-02 | 4.1 | 254.08 | $Al_2(SO_4)_3$ | 60 mmol / L | 65.1 |
| **m-0614a-02 | 8.59 | 240.23 | $MgCl_2$ | 10 mmol / L | 65.7 |
| **m-0614a-04 | 8.62 | 248.14 | $MgCl_2$ | 10 mmol / L | 67.7 |

* pH lowered by the presence of aluminum sulfate
** Sodium Hydroxide was also added to increase the pH to 9 – 9.5.

## 13.2  Appendix - Details of December 2004 field silica extraction work.

(*The work described here relates to Subtask 2.1.2 of PIR-00-003.*)

**Table A13.2-1**.  Matrix of operating conditions under which ultrafiltered concentrates were obtained.

| Time | 10:50 | 11:15 | 11:21 | 11:34 | 12:30 | 12:50 | 13:17 | 13:30 | 14:00 | 14:31 | 14:47 | (flush) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant Feed (PSI) | 68 | | | 132 | 125 | 128 | 128 | 125 | 128 | 128 | 128 | 0 |
| Feed Temperature (Centigrade) | 18 | | | 68 | 72 | 72 | 71 | 71 | 71 | 71 | 71 | |
| Pump Supply Pressure to Inlet Filters | 15 | | | | 45 | 45 | 45 | 44 | 45 | 45 | 45 | 0 |
| Pump Supply Pressure past Filters | 8.2 | | | | 41 | 41 | 41 | 41 | 41 | 41 | 41 | 0 |
| Supply Flow (GPM) | | | | | | 10+ | 10+ | 10+ | 10+ | 10 | 9.8 | 1.5 |
| Flow Control Valve, Vessel (GPM) | 7 | | | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 4.8 | 10 |
| Flow Control Valve, Recycle (GPM) | | | | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 | 0 |
| Conc. Recycle Flow (GPM) | 0 | | | 2.9 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 0 |
| Conc. Vessel (GPM) | 1.2 | | | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ |
| Permeate Flow (GPM) | 0 | | | 3 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.3 | 2.3 | 0 |
| Bypass Flow (GPM) | 0 | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Perm Pressure (past RO elements) (PSI) | 5 | 20 | | 20 | 20 | 20 | 20 | 20 | 15 | 17 | 16 | low |
| Conc. Pressure (past RO elements) (PSI) | 40 | | | 80 | 85 | 85 | 85 | 85 | 85 | 87 | 87 | 70 |
| Conc. Recycle (PSI) | | 230 | 325 | 265 | 300 | 315 | 335 | 345 | 355 | 378 | 390 | 90 |
| CAT Pump Pressure (PSI) | | 240 | 350 | 278 | 305 | 320 | 345 | 360 | 380 | 395 | 400 | 0 |
| Hedland Flow Meter GPM | | 7.9 | 7.3 | | 7.3 | 7.4 | 7.3 | 7.3 | 7.2 | 7.1 | 7.2 | 7.1 |
| Hedland Totalizer (GPM) | | | 92 | | | 748 | 936 | 1057 | 1244 | 1466 | 1585 | |
| Vessel Temperature, Upper (Centigrade) | 52 | 60 | 61 | 65 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 66 |
| Vessel Temperature, Lower (Centigrade) | 52 | 60 | 61 | 66 | 70 | 71 | 71 | 70 | 70 | 71 | 71 | 59 |
| Vessel Pressure (PSI) | 40 | 21 | 24 | | 52 | 54 | 56 | 53 | 53 | 54.5 | 55 | 70 |
| Vessel Flow (L/m) | 4.77 | 5.5 | 5.9 | 11.2 | 11.6 | 11.79 | 11.6 | 11.7 | 11.58 | 11.71 | 11.82 | 16.21 |
| Vessel Totalizer (L/m) | | | | | 995 | 1225 | 1534 | 1737 | 2051.6 | 2412 | 2608 | |
| PCI Inlet Pressure (PSI) | 18 | 16 | | 43 | 44 | 45 | 42 | 42 | 42 | 47 | 45 | |
| PCI Outlet Pressure (PSI) | 18 | 20 | | 45.5 | 46 | 47 | 46 | 46 | 46 | 47 | 47 | |
| PCI Permeate Flow (GPM) | 1.2 | 1.6 | | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | 2+ | | |
| Agitator Speed (%) | | | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | 38 | off |
| Notes | 1 | | | 2 | 3 | | | | | | | 4 |

Note 1: RO Filters in place, Pump Off
Note 2: Measured ultrafilter collection flow at 65 ml/m
Note 3: Increased supply pressure regulator to 45 psi
Note 4: Feed Disconnected, Permeate flush.  Pump had more vibration than with pressurized feed

<u>Results of refractometry and hydrometry on colloidal silica samples collected during December 2004.</u>

(*The work described here relates to Subtask 2.1.2 and 2.1.3 of PIR-00-003.*)

**Table A13.2-2**. Comparison between several field samples and two industrial colloidal silica samples[*] with respect to several indicative parameters.

|  | T ($^o$C) | Conductivity (mS) | RI | Specific Gravity |
|---|---|---|---|---|
| Nanosol® 4020S | 24.1 | 4.02 | 1.367 | > 1.220 |
| Nanosol® 5050S | 24.2 | 2.57 | ~1.371 | > 1.220 |
| Geothermal Feed Water | 24.2 | 1.667 | < 1.33 | 1.0002 |
| RO Permeate | 24.1 | 1.021 | < 1.33 | 1.0001 |
| RO Concentrate | 24.2 | 1.610 | < 1.33 | 1.105** |

* The two Nanosol® samples were provided by Mark Jarand of Colloidal Solutions.

** After centrifugation

**Table A13.2-3**. Solution density values of several ultrafiltered concentrates measured in the field using a hydrometer.

|  | T ($^o$C) | Conductivity (mS) | pH | Specific gravity$_f$[#] |
|---|---|---|---|---|
| 10:50 | 26.7 | 1.677 | 6.8 | - |
| 11:34 | 31.4 | 2.86 | 6.78 | 1.0000 |
| Con. Initial | 30.4 | 2.91 | 6.53 | 1.0020 |
| Con. 1 | 31.1 | 2.9 | - | 1.0030 |
| Con. 2 | - | - | - | 1.0030 |
| Con. 3 | 29.2 | 2.87 | 6.82 | 1.0010 |
| Con. 4 | 34.2 | 2.73 | 6.52 | - |

NB: The two earliest samples were collected by increasing the concentrate flow rate, whereas the four later samples were collected over a longer period of time using a much slower flow rate. The latter method yields higher concentrations of silica and more closely mimics a "batch mode" of operation because it allows for greater recycling of the solution before it is sampled. Future extractions using ultrafiltration will operate under a batch mode to further increase the efficacy of the ultrafilter.

13.3 <u>Appendix - Analytical data for silica precipitates and treated geothermal fluids.</u>

**Table A13.3-1**. Average detection limits of elements analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by Activation Laboratories for the aqueous samples collected during all field excursions. Values reported are in µg/ L.

A) ICP-MS, values in mg/ L

| | | | | |
|-----|-------|-----|-------|
| Ag | 0.05 | Na | 5 |
| Al | 2 | Nb | 0.005 |
| As | 0.03 | Nd | 0.004 |
| Au | 0.002 | Ni | 0.2 |
| B | 1 | Os | 0.002 |
| Ba | 0.1 | P | |
| Be | 0.05 | Pb | 0.1 |
| Bi | 0.01 | Pd | 0.01 |
| Br | 3 | Pr | 0.001 |
| Ca | 50 | Pt | 0.01 |
| Cd | 0.01 | Rb | 0.01 |
| Ce | 0.002 | Re | 0.001 |
| Co | 0.005 | Rh | 0.02 |
| Cr | 0.5 | Ru | 0.01 |
| Cs | 0.002 | S | |
| Cu | 0.1 | Sb | 0.01 |
| Dy | 0.001 | Sc | 1 |
| Er | 0.001 | Se | 0.2 |
| Eu | 0.001 | Si | 50 |
| Fe | 5 | Sm | 0.002 |
| Ga | 0.01 | Sn | 0.05 |
| Gd | 0.002 | Sr | 0.04 |
| Ge | 0.01 | Ta | 0.001 |
| Hf | 0.002 | Tb | 0.001 |
| Hg | 0.2 | Te | 0.01 |
| Ho | 0.001 | Th | 0.001 |
| In | 0.001 | Ti | 0.1 |
| In | 1 | Tl | 0.005 |
| Ir | 0.002 | Tm | 0.001 |
| K | 10 | U | 0.001 |
| La | 0.001 | V | 0.05 |
| Li | 0.1 | W | 0.02 |
| Lu | 0.001 | Y | 0.003 |

B) IC, values in ppm

| | |
|-------------------|-------|
| Fluoride (F) | 0.005 |
| Chloride (Cl) | 0.02 |
| Bromide (Br) | 0.05 |
| Nitrite ($NO_4$) | 0.005 |
| Nitrate ($NO_3$) | 0.005 |
| Phosphate ($P_2O_5$) | 0.02 |
| Sulfate ($SO_4$) | 0.05 |

| Mg | 1 | | Yb | 0.001 |
|----|------|--|----|-------|
| Mn | 0.05 | | Zn | 0.5 |
| Mo | 0.1 | | Zr | 0.01 |

**Table A13.3-2**. Elemental concentrations of silica samples collected during the June 2002 field work. Only those elements detected in at least one sample are reported. Values measured by ICP-MS unless otherwise noted.

| | | M-0612A-02 | M-0612A-04 | M-0612A-06 | M-0613A-02 | M-0614A-02 | M-0614A-04 | M-BULK FLUID |
|---|---|---|---|---|---|---|---|---|
| Major Elements, ppm | Al | -- | -- | 0.12 | 12.80 | 1.05 | 1.31 | 0.13 |
| | Ca | 3.32 | 3.65 | 4.98 | 7.00 | 4.92 | 6.98 | 5.17 |
| | Fe | -- | -- | -- | 1.08 | -- | -- | -- |
| | K | 53.20 | 37.10 | 38.90 | 33.10 | 38.20 | 38.90 | 35.30 |
| | Mg | 35.10 | 37.70 | 0.95 | 0.23 | 0.17 | 0.23 | 0.22 |
| | Na | 1080 | 1270 | 966 | 1210 | 995 | 1250 | 314 |
| | Si | 1.07 | 1.03 | 121.40 | 99.30 | 116.20 | 126.00 | 106.00 |
| | Ti | -- | -- | 0.017 | 0.014 | 0.016 | 0.019 | 0.010 |
| Trace Elements, ppb | As | -- | -- | 1420.00 | 1130.00 | 1390.00 | 1480.00 | 1330.00 |
| | Ba | 1.27 | 1.24 | 14.34 | 10.92 | 6.14 | 6.17 | 13.30 |
| | Be | -- | -- | 1.56 | 1.34 | -- | -- | 2.09 |
| | Br | 505.53 | 494.61 | 603.40 | 513.44 | 567.35 | 623.81 | 565.83 |
| | Cs | 301.85 | 311.57 | 324.43 | 268.82 | 322.28 | 334.75 | 315.38 |
| | Cu | -- | -- | -- | -- | -- | -- | 21.15 |
| | Ga | -- | -- | 2.36 | 0.49 | 2.49 | 2.78 | 1.62 |
| | Ge | -- | -- | 43.47 | 33.79 | 40.59 | 44.17 | 40.02 |
| | Hf | -- | -- | -- | 0.03 | -- | -- | -- |
| | I | 581.26 | 571.22 | 631.11 | 524.45 | 647.78 | 691.83 | 593.49 |
| | La | -- | -- | 0.01 | 0.03 | 0.03 | 0.02 | 0.26 |
| | Li | 2200 | 2270 | 2300 | 1780 | 2240 | 2330 | 2120 |
| | Mn | -- | -- | 0.02 | 0.03 | -- | -- | 0.03 |
| | Mo | 2.22 | -- | 2.95 | 5.88 | 4.51 | 4.02 | 16.01 |
| | Nb | -- | -- | -- | -- | -- | -- | 0.09 |
| | Ni | 32.79 | 43.32 | -30.00 | 77.10 | 36.40 | 102.80 | 30.11 |
| | Pd | -- | -- | -- | 1.02 | 1.02 | -- | -1.00 |
| | Rb | 270.56 | 281.51 | 304.28 | 248.82 | 293.61 | 309.60 | 287.11 |
| | Sb | 18.50 | 17.38 | 40.37 | 11.76 | 78.03 | 64.74 | 35.18 |
| | Sc | -- | -- | 21.27 | 15.27 | 16.82 | 18.80 | 13.00 |
| | Se | 20.01 | -- | -- | -- | -- | -- | -- |
| | Sr | 13.70 | 15.29 | 116.48 | 131.15 | 151.48 | 158.65 | 161.89 |
| | Te | -- | -- | -- | 0.19 | -- | 0.12 | -- |
| | Th | -- | -- | 0.041 | 0.036 | 0.032 | -- | 0.011 |
| | U | -- | -- | -- | 0.01 | -- | -- | -- |

| W | 98.82 | 93.04 | 146.50 | 17.10 | 136.80 | 145.37 | 155.81 |
|---|---|---|---|---|---|---|---|
| Zn | -- | -- | -- | 22.20 | -- | -- | -- |
| Zr | -- | -- | 0.38 | -- | 0.15 | 0.17 | -- |
| SO4$^{2-}$ | 101.90 | 103.77 | 106.67 | 459.89 | 105.05 | 104.91 | 89.38 |

1    Concentration below detection limit.
2    Measured by Ion Chromatography (IC), values in ppm.

**Table A13.3-3**. Elemental concentrations of silica samples collected during the July-August 2002 field excursion. Only those elements detected in at least one sample are reported. Values measured by ICP-MS unless otherwise noted.

| | | M-0802-HW2 | M-0802-HW3 | DOWNSTREAM | HOT POND DISCHARGE |
|---|---|---|---|---|---|
| Major Elem., ppm | K | 33.5 | 35.3 | 41.6 | 42.1 |
| | Mg | -- [1] | -- | 0.28 | 0.27 |
| | Na | 354 | 374 | 477 | 479 |
| | Si | 69.8 | 71.2 | 67.6 | 69.7 |
| | Ti | 0.014 | 0.013 | 0.013 | 0.011 |
| Trace Elements, ppb | As | 1530 | 1560 | 1940 | 1920 |
| | Ba | 10.94 | 12.47 | 12.38 | 12.66 |
| | Br | 545.20 | 554.25 | 696.79 | 699.21 |
| | Cd | -- | -- | -- | 4.41 |
| | Cs | 358.60 | 368.36 | 434.20 | 436.41 |
| | Cu | -- | 69.91 | -- | -- |
| | Ga | 1.30 | 1.69 | 1.16 | 1.20 |
| | Ge | 45.67 | 44.92 | 58.21 | 58.22 |
| | I | 459.88 | 466.95 | 419.22 | 332.98 |
| | Li | 2180 | 2310 | 2890 | 2880 |
| | Mn | 12.98 | 14.91 | -- | -- |
| | Mo | -- | -- | 77.982 | 1830 |
| | Pd | 1.228 | -- | -- | -- |
| | Rb | 325.78 | 340.35 | 401.04 | 392.63 |
| | Sb | 228.66 | 138.38 | 126.56 | 131.25 |
| | Sr | 123.29 | 130.12 | 176.24 | 174.85 |
| | W | 235.84 | 234.64 | 299.73 | 311.21 |
| | Zr | -- | -- | 3.61 | -- |
| | Cl [2] | 301 | 301 | 369 | 369 |
| | SO4 [2] | 110 | 110 | 146 | 150 |

1    Concentration below detection limit.
2    Measured by IC, values in ppm.

**Table A13.3-4**. Elemental concentrations of reverse osmosis fluid samples collected during the October 2002 field excursion. Only those elements detected in at least one sample are reported. Values measured by ICP-MS unless otherwise noted.

| | | 10/1 RO-P [1] | 10/1 RO-C [2] | 10/4 RO-P | 10/4 RO-C | 10/4 RO-C2 | 10/4 RO-P2 |
|---|---|---|---|---|---|---|---|
| Major Elem., ppm | Al | -- [3] | 0.24 | -- | 0.24 | -- | -- |
| | K | -- | 87.30 | -- | 79.90 | 85.60 | 84.20 |
| | Mg | -- | 1.54 | -- | 0.41 | 0.30 | 0.44 |
| | Na | 3.66 | 994 | 14.50 | 920 | 1000 | 976 |
| | Si | -- | 219 | -- | 192 | 218 | 204 |
| | Ti | -- | 0.039 | -- | 0.035 | 0.037 | 0.031 |
| Trace Elements, ppb | As | 32.05 | 3930 | 87.07 | 3700 | 3870 | 3800 |
| | Ba | -- | 40.79 | -- | 32.56 | 40.45 | 34.37 |
| | Br | -- | 1570 | -- | 1530 | 1530 | 1520 |
| | Cs | 3.26 | 881.72 | 13.11 | 818.42 | 884.25 | 866.31 |
| | Ga | 1.56 | 4.71 | -- | 2.08 | 2.54 | 1.57 |
| | Ge | -- | 118.33 | -- | 117.86 | 119.09 | 117.44 |
| | I | -- | 1320 | -- | 1260 | 1320 | 1260 |
| | La | -- | -- | -- | -- | -- | 0.15 |
| | Li | -- | 5950 | 102.91 | 5550 | 5600 | 5530 |
| | Mn | -- | 81.76 | -- | 77.81 | 79.74 | 77.24 |
| | Mo | -- | 13.45 | -- | -- | -- | -- |
| | Rb | 2.96 | 803.19 | 11.55 | 756.80 | 810.17 | 787.97 |
| | Sb | -- | 230.63 | 2.15 | 100.94 | 120.88 | 117.66 |
| | Sr | -- | 407.11 | -- | 367.81 | 400.93 | 389.14 |
| | W | 4.73 | 631.90 | 3.98 | 566.98 | 624.28 | 616.90 |
| | Zr | 3.13 | -- | -- | -- | -- | -- |
| | Cl [4] | 1.43 | 754 | 1.34 | 725 | 772 | 748 |
| | SO$_4$ [4] | 0.24 | 328 | 0.13 | 296 | 326 | 320 |

1    RO-P = Permeate.
2    RO-C = Concentrate.
3    Concentration below detection limit.
4    Measured with ion chromatography, values in ppm.

**Table A13.3-5**.  Elemental concentrations of precipitated silica samples collected during the October 2002 field excursion.  Only those elements detected in at least one sample are reported.  Values measured by ICP-MS unless otherwise noted.

| | | CLEAN [1] (H+) | CLEAN (H+) [2] | CLEAN (OH-) [2] | DIRTY [1] (H+) | DIRTY (OH-) |
|---|---|---|---|---|---|---|
| Major Elem., ppm | Al | -- [3] | -- | 0.36 | -- | -- |
| | Mg | 0.18 | 0.12 | 0.17 | -- | -- |
| | Na | 0.51 | -- | 2630 | 1.77 | 2470 |
| | Si | -- | -- | 49.70 | -- | 30.50 |
| Trace Elements, ppb | As | 4.07 | 3.79 | 12.98 | 32.47 | 34.09 |
| | Cs | 3.56 | 3.54 | 2.49 | 1.44 | 1.09 |
| | Cu | -- | -- | -- | 26.20 | -- |
| | Ga | -- | -- | 5.23 | 14.89 | 2.51 |
| | Ge | -- | -- | 1.26 | -- | 1.02 |
| | In | -- | -- | -- | 3.12 | -- |
| | Rb | 0.64 | 0.63 | 1.28 | 1.43 | 0.70 |
| | Sb | -- | -- | 29.32 | 1.43 | 46.87 |
| | U | -- | -- | -- | 0.15 | -- |
| | W | -- | -- | 4.55 | -- | 3.35 |
| | Cl [4] | 383 | 381 | -- | 382 | -- |

1       A grayish tint was observed initially on the precipitates ("Dirty silica"). The samples collected after
            shutting the system down and looking for pollutants appeared
            pure white ("Clean silica").
2       Both the Clean and the Dirty silica were divided into two sets and each set was digested either in a
            weak acid (H+) or weak base (OH-).
3       Concentration below detection limit.
4       Measured by IC, values in ppm.

**Table A13.3-6**. Elemental concentrations of silica precipitates collected after adding 100 ppm XP-251 during the October 2002 field excursion. Only those elements detected in at least one sample are reported. Values measured by ICP-MS unless otherwise noted.

| | | 8.5 min [1] | 30 min. [1] | 30 min. (2) | 600 ppm $SiO_2$ [2] | + 50 mmol $MgCl_2$ [3] |
|---|---|---|---|---|---|---|
| Major Elem., ppm | K | 83.4 | 83.2 | 84.3 | 83.4 | 79.8 |
| | Mg | 0.42 | 0.42 | 0.53 | 0.45 | 417 |
| | Na | 958 | 941 | 958 | 964 | 920 |
| | Si | 142 | 140 | 185 | 196 | 133 |
| | Ti | 0.024 | 0.024 | 0.031 | 0.033 | 0.022 |
| Trace Elements, ppb | As | 3710 | 3730 | 3820 | 3760 | 3640 |
| | Ba | 32.35 | 31.42 | 33.63 | 31.43 | 55.17 |
| | Br | 1580 | 1510 | 1620 | 1540 | 1470 |
| | Cs | 834.88 | 838.11 | 861.86 | 829.62 | 814.03 |
| | Ga | -- [4] | -- | -- | 1.26 | -- |
| | Ge | 113.70 | 112.32 | 121.51 | 116.05 | 109.25 |
| | I | 1270 | 1270 | 1360 | 1260 | 1210 |
| | Li | 5720 | 5780 | 5850 | 5680 | 5380 |
| | Mn | 71.47 | 70.50 | 78.64 | 75.62 | 72.86 |
| | Ni | -- | -- | 54.34 | -- | -- |
| | Rb | 772.67 | 771.54 | 787.61 | 778.07 | 745.72 |
| | Sb | 103.88 | 102.70 | 115.91 | 103.29 | 99.71 |
| | Sr | 378.36 | 374.67 | 389.41 | 380.87 | 365.70 |
| | W | 591.45 | 619.28 | 623.58 | 601.49 | 599.37 |
| | Zr | -- | -- | -- | 11.81 | -- |
| | Cl [5] | 718 | 728 | 772 | 728 | 2030 |
| | $SO_4$ [5] | 286 | 287 | 312 | 297 | 280 |

1    Samples of the slurry were collected 8.5 minutes and 30 minutes after the XP-251 was added.
2    XP-251 was added to a solution which already had approximately 600 ppm SiO2 in solution.
3    XP-251 was added to a solution in which 50 mmol MgCl2 was also added.
4    Concentration below detection limit.
5    Measured by IC, values in ppm.

**Table A13.3-7**.  Elemental concentrations of precipitated silica samples collected after adding various concentrations (50, 100, and 200 ppm) of XP-251 during the October 2002 field excursion.  Only those elements detected in at least one sample are reported.  Values measured by ICP-MS and reported in ppb, unless otherwise noted.

|  | 50 ppm (H+) [1] | 50 ppm (OH-) [1] | 100 ppm (H+) | 100 ppm (OH-) | 200 ppm (H+) | 200 ppm (OH-) |
|---|---|---|---|---|---|---|
| As | 6.29 | 8.66 | 5.28 | 4.91 | 3.64 | 7.73 |
| Cs | 2.91 | 3.59 | 1.68 | 2.13 | 1.93 | 3.49 |
| Cu | 41.47 | -- | -- | -- | -- | -- |
| Ga | -- [2] | 2.95 | 1.90 | 1.70 | 23.04 | 51.55 |
| In | -- | -- | -- | -- | 3.61 | 6.38 |
| **Na [3]** | **0.776** | **2490** | **0.924** | **2440** | **1.29** | **2640** |
| Pb | -- | -- | -- | 17.29 | -- | -- |
| Rb | 1.47 | 1.60 | 0.98 | 0.92 | 1.42 | 1.53 |
| Sb | 2.98 | 22.92 | 2.06 | 16.04 | -- | 20.38 |
| **Si [3]** | **--** | **38.5** | **--** | **33.1** | **--** | **39.1** |
| W | 5.61 | 4.14 | -- | 2.11 | -- | -- |
| Cl [4] | 380 | -- | 386 | -- | 372 | -- |

1       All precipitated silica samples were divided into two sets and each set was digested either in a  weak
          acid (H+) or weak base (OH-).
2       Concentration below detection limit.
3       Values in **bold** are Major Elements and are reported as ppm.
4       Measured by IC, values in ppm.

**Table A13.3-8**. Elemental concentrations of samples treated with Reverse Osmosis during the December 2002 field excursion. Only those elements detected in at least one sample are reported. Values measured by ICP-MS. Duplicate analyses of the brine are given.

| | | RO-P [1] | RO-C [2] | BRINE INPUT | BRINE INPUT (DUP) |
|---|---|---|---|---|---|
| Major Elements, ppm | Al | 0.15 | 0.27 | 0.25 | 0.19 |
| | Ca | -- [3] | 2.54 | -- | -- |
| | Fe | 0.45 | -- | -- | 1.43 |
| | K | 1.96 | 65.40 | 32.70 | 30.30 |
| | Mg | -- | 0.37 | 0.21 | 0.19 |
| | Na | 23.8 | 727 | 360 | 329 |
| | Si | -- | 193 | 100 | 91.5 |
| | Ti | -- | 0.013 | -- | -- |
| Trace Elements, ppb | As | 36.45 | 2800 | 1370 | 1250 |
| | Ba | -- | 30.98 | 8.52 | 7.63 |
| | Be | -- | 4.83 | 1.99 | -- |
| | Br | -- | 1080 | 478.85 | 443.74 |
| | Cs | 23.89 | 697.41 | 333.68 | 311.16 |
| | Cu | 22.19 | -- | 131.28 | 32.31 |
| | Dy | -- | 0.02 | -- | -- |
| | Ga | -- | 2.94 | 1.41 | 1.32 |
| | Ge | -- | 83.49 | 41.19 | 37.47 |
| | Hf | -- | 0.04 | -- | 0.04 |
| | I | -- | 892.04 | 332.52 | 281.76 |
| | Li | 110.08 | 3810 | 1870 | 1720 |
| | Mn | -- | 41.25 | 21.79 | 16.55 |
| | Mo | -- | 4.60 | 2.43 | 1.71 |
| | Ni | 52.88 | -- | 911.76 | 595.90 |
| | Pd | -- | 1.38 | -- | -- |
| | Rb | 19.74 | 565.60 | 281.16 | 257.12 |
| | Re | -- | 0.011 | -- | -- |
| | Sb | -- | 47.22 | 87.85 | 79.62 |
| | Sc | -- | 19.07 | -- | -- |
| | Sm | 0.046 | -- | -- | -- |
| | Sr | -- | 304.79 | 143.59 | 133.14 |
| | Te | 0.22 | 0.25 | -- | -- |
| | Th | -- | 0.012 | -- | -- |
| | W | 2.53 | 389.98 | 179.51 | 168.55 |

|     |     |       |        |        |        |
| --- | --- | ----- | ------ | ------ | ------ |
|     | Yb  | --    | 0.011  | 0.021  | --     |
|     | Zn  | 87.97 | 162.38 | 550.22 | 509.38 |
|     | Zr  | 0.57  | --     | --     | --     |

| IC [4] | Br  | --   | 1.16 | 0.59 | 0.59 |
| ------ | --- | ---- | ---- | ---- | ---- |
|        | Cl  | 1.37 | 501  | 235  | 238  |
|        | F   | 0.35 | 23.3 | 11.5 | 11.2 |
|        | SO4 | 0.94 | 224  | 115  | 116  |

1    RO-P = Permeate.
2    RO-C = Concentrate.
3    Concentration below detection limit.
4    All values including Br and below on the list were measured by IC, values in ppm.

**Table A13.3-9**. Elemental concentrations of fluid samples treated with Ion Exchange (IX) resins. Only those elements detected in at least one sample are reported. Values measured by ICP-MS unless otherwise noted. IX work was funded by DOE Geothermal Technologies Program and is not discussed further in this report.

| | | 12/13 IX INPUT (1) | 12/13 IX INPUT (2) | 12/13IX #1 | 12/13 IX #2 | 12/13 IX #3 | 12/13 IX #4 | 12/13 IX #5 |
|---|---|---|---|---|---|---|---|---|
| **Major Elem., ppm** | Al | 0.19 | 0.15 | 0.39 | 0.18 | 0.16 | 0.13 | 0.13 |
| | Ca | -- [1] | -- | 2.12 | -- | -- | -- | -- |
| | K | 62.70 | 58.20 | 42.30 | 50.90 | 62.00 | 61.60 | 65.70 |
| | Mg | 0.38 | 0.43 | 0.37 | -- | 0.11 | -- | -- |
| | Na | 705 | 649 | 479 | 582 | 709 | 697 | 734 |
| | Si | 110 | 98 | 40 | 57 | 74 | 79 | 84 |
| **Trace Elements, ppb** | As | 2740 | 2530 | 1700 | 2110 | 2610 | 2620 | 2780 |
| | Au | 0.049 | 0.063 | 0.032 | 0.026 | -- | -- | 0.027 |
| | Ba | 18.56 | 15.79 | -- | -- | -- | -- | 1.92 |
| | Br | 1100 | 994.93 | 758.08 | 911.57 | 1070 | 1070 | 1110 |
| | Cd | -- | 0.34 | 0.75 | -- | 0.89 | -- | -- |
| | Ce | -- | -- | 0.095 | -- | -- | -- | -- |
| | Cr | 29.46 | 20.52 | 18.91 | 12.99 | -- | -- | -- |
| | Cs | 663.43 | 593.34 | 425.12 | 512.62 | 643.32 | 624.27 | 662.34 |
| | Cu | -- | 158.00 | 112.73 | 34.88 | -- | -- | 21.38 |
| | Er | -- | 0.01 | -- | -- | -- | -- | -- |
| | Eu | -- | -- | -- | -- | -- | 0.020 | -- |
| | Ga | -- | -- | 0.22 | 0.11 | -- | -- | -- |
| | Ge | 83.84 | 76.49 | 50.74 | 61.33 | 74.44 | 75.23 | 79.43 |
| | Hf | 0.037 | -- | 0.11 | -- | -- | 0.13 | -- |
| | I | 931.66 | 810.74 | 580.69 | 725.36 | 902.95 | 879.20 | 896.26 |
| | Li | 3780 | 3400 | 2230 | 2820 | 3510 | 3440 | 3630 |
| | Mo | 5.13 | 26.23 | 2.86 | 3.13 | 4.92 | 4.33 | 4.79 |
| | Nd | -- | 0.14 | 0.08 | -- | -- | -- | -- |
| | Ni | -- | 101.29 | 400.48 | 407.17 | -- | -- | -- |
| | Pd | 1.08 | -- | -- | 1.49 | 1.48 | 1.06 | -- |
| | Rb | 546.65 | 499.51 | 364.05 | 434.99 | 532.05 | 526.12 | 559.60 |
| | Sb | 47.10 | 44.07 | 28.04 | 36.22 | 43.96 | 43.14 | 47.33 |
| | Sc | 11.72 | 10.02 | -- | -- | -- | -- | -- |
| | Sr | 226.06 | 183.61 | 3.63 | -- | -- | -- | -- |
| | Th | 0.017 | -- | 0.012 | -- | -- | -- | -- |
| | V | 8.94 | 6.68 | 5.97 | -- | -- | -- | -- |
| | W | 363.92 | 346.35 | 244.57 | 303.09 | 369.76 | 362.11 | 391.17 |

| Yb | -- | -- | -- | -- | -- | -- | -- |
|---|---|---|---|---|---|---|---|
| Zn | 476.00 | 794.96 | 777.78 | 59.46 | 776.22 | 66.27 | 71.69 |
| Zr | -- | -- | 0.90 | -- | -- | 1.86 | -- |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| IC (2) | Br | 1.45 | 1.55 | 1.44 | 1.21 | 0.92 | 0.89 | 1.07 |
| | Cl | 505 | 501 | 506 | 504 | 502 | 503 | 503 |
| | F | 21.7 | 23.3 | 18.3 | 20.5 | 20.9 | 19.9 | 21.4 |
| | SO4 | 227 | 228 | 229 | 225 | 226 | 226 | 226 |

1     Concentration below detection limit.

2     All values including Br and below on the list were measured by IC, values in ppm.

**Table A13.3-10a**.  Elemental concentrations of precipitated silica samples comparing the raw samples with sample leached with either De-Ionized water (DI Rinse) or with a weak hydrochloric acid (Acid Rinse).  Samples collected and treatments applied during December 2002.  Only those elements detected in at least one sample are reported.  Values measured by ICP-MS and Instrumental Neutron Activation Analysis (INAA) reported in ppm, unless otherwise noted; values measured by X-ray Fluorescence Spectroscopy (XRF) reported in weight percent (wt. %) or ppm.

|  |  | Raw | DI Rinse | Acid Rinse |
|---|---|---|---|---|
| INAA | Au [2] | 70 | 64 | 47 |
|  | As | 450 | 304 | 162 |
|  | Br | 13.5 | 8.1 | 1.5 |
|  | Co | 1.9 | 1.6 | 1.1 |
|  | Cr | 21.5 | 2.3 | 7.4 |
|  | Cs | 20.7 | 17.6 | 4.6 |
|  | Hg | 4 | 4 | 1 |
|  | Mo | 20 | 18 | 10 |
|  | Sb | 348 | 332 | 197 |
|  | Sc | 0.34 | 0.28 | 0.19 |
|  | W | 31 | 26 | 15 |
|  | La | 0.34 | 0.16 | 0.25 |
|  | Sm | -- [1] | 0.02 | -- |
|  | Mass [3] | 0.531 | 0.539 | 0.837 |
| ICP-MS | Cu | 13.76 | 13.25 | 9.89 |
|  | Ni | 4.17 | 2.68 | 2.16 |
|  | Zn | 125.75 | 175.36 | 46.40 |
|  | S [4] | 0.20 | 0.14 | 0.03 |
| XRF (wt. %) | $SiO_2$ | 76.66 | 72.59 | 45.44 |
|  | $Al_2O_3$ | 0.26 | 0.23 | 0.14 |
|  | $Fe_2O_3$ | 0.17 | 0.16 | 0.09 |
|  | MnO | 0.008 | 0.008 | 0.005 |
|  | MgO | 0.1 | 0.09 | 0.02 |
|  | CaO | 0.13 | 0.11 | 0.01 |
|  | $Na_2O$ | 0.9 | 0.06 | 0.01 |
|  | $K_2O$ | 0.12 | 0.04 | -- |
|  | $TiO_2$ | 0.005 | -- | -- |
|  | $P_2O_5$ | 0.02 | 0.02 | 0.01 |
|  | LOI [5] | 21.91 | 26.8 | 54.53 |
|  | TOTAL | 100.27 | 100.1 | 100.27 |
| XRF (ppm) | Ba | 2 | 2 | 2 |
|  | Sr | 33 | 18 | 5 |
|  | Be | 19 | 18 | 11 |
|  | V | 10 | 6 | 5 |

1  Concentration below detection limit.
2  Values in ppb.
3  Value in g.
4  Value in %.
5  LOI = Loss on Ignition

**Table A13.3-10b**.  Elemental concentrations of leachates collected during treatment of precipitated silica samples reported in Table 7.4-10a.  Only those elements detected in at least one sample are reported.  Values measured by ICP-MS reported in ppb, unless otherwise noted.

| | L-1 | L-2 | | | L-1 | L-2 |
|---|---|---|---|---|---|---|
| **Al** [1] | **0.075** | **0.0040** | | **Na** | **16.1** | **14.2** |
| As | 287.46 | 291.21 | | Nd | 0.012 | -- |
| Au | 0.019 | 0.010 | | Ni | 4.49 | 10.34 |
| Ba | 3.17 | 0.13 | | Pb | 1.75 | -- |
| Be | 2.46 | --[2] | | Pd | 0.35 | 0.014 |
| Br | 136.30 | 12.20 | | Pr | 1.18E-03 | -- |
| **Ca** | **1.65** | **0.101** | | Rb | 19.22 | 5.90 |
| Cd | 0.15 | -- | | Re | 0.0013 | 0.0014 |
| Ce | 0.016 | -- | | Ru | 0.012 | -- |
| Co | 0.16 | 0.013 | | Sb | 13.05 | 21.81 |
| Cr | -- | 0.60 | | **Si** | **0.31** | **8.46** |
| Cs | 30.15 | 4.49 | | Sm | 0.0026 | -- |
| Cu | 4.36 | -- | | Sn | 0.49 | -- |
| **Fe** | **0.17** | -- | | Sr | 25.85 | 3.76 |
| Ga | 4.23 | 0.090 | | **Ti** | **2.19E-04** | **5.67E-04** |
| Gd | 0.017 | -- | | Tl | 0.097 | -- |
| Ge | 2.60 | 1.30 | | U | 1.92E-03 | -- |
| Hg | 0.37 | -- | | V | -- | 0.44 |
| I | 32.18 | 16.61 | | W | 10.12 | 8.52 |
| In | 0.71 | 0.01 | | Y | 3.36E-03 | -- |
| **K** | **1.82** | **0.98** | | Zn | 328.00 | 22.91 |
| La | 0.010 | -- | | Zr | 0.020 | -- |
| Li | 78.07 | 68.40 | | Cl [3] | 4170 | 9.92 |
| **Mg** | **0.96** | **0.17** | | F | -- | 0.27 |
| Mn | 20.16 | 0.12 | | SO4 | -- | 3.77 |
| Mo | 3.79 | 3.12 | | | | |

1      Values in **bold** are Major Element and are reported as ppm.
2      Concentration below detection limit.
3      All values including Cl and below on the list were measured by IC.

### 13.4 Appendix - Silica Drying test results

Work carried out by Amanda Ranier, LLNL Summer Scholar during the summer of 2003

Introduction

(*The work described here relates to Subtask 2.1.1 of PIR-00-003.*)

The purpose of the project was to investigate how changes in drying technique and pH level affected the surface properties, primarily surface area, of precipitated silica. This project is an addendum to the Geothermal Project; in this part, the intent was to find a marketable use for the silica collected at the geothermal site, particularly for commercial or industrial applications.

Silica, of varying forms, is used in a wide variety of areas including battery separators and industrial rubber, as well as the tire and food industries. Two of the major producers of silica include PPG Industries and Degussa Corporation. Each manufacturer generates a wide range of silica products to suit a multitude of applications. Silicas are classified by several characteristics including pH, absorption, median agglomerate size, bulk density, and the Brunauer, Emmet, and Teller (BET) method for measuring surface area. The importance of each characteristic is dependent on the field of use. For example, PPG Industries produces silica products for tire industry (140-239 $m^2$/g), industrial rubber (35-250 $m^2$/g), footwear industry (35-250 $m^2$/g), and carrier applications (150 $m^2$/g) [1]. The main use investigated here pertained to applications in tires. Silica is used as a reinforcing filler in the tire industry[1] and makes up about 30% of the modern tire tread recipe.[2] The addition of silica is reported to increase the structural integrity of the tires, improve rolling resistance, and wet traction.[1] Nitrogen BET surface area is reported to be an accurate predictor of the physical performance of silica-filled rubber compounds.[3]

Materials and Methods

Initially, fifteen variable-temperature samples were made using 5.00 g of Degussa Ultrasil® VN3SP synthetic, amorphous, precipitated silica and approximately 225 mL of milli-Q water. The samples were stored in plastic bottles and left on a shaker to ensure that the silica did not turn into a gel. The pH of the samples was measured and recorded, and then the samples were filtered through a 0.1-micron filter using vacuum filtration. Each sample was oven dried at a specific temperature in a glass dish. The samples were dried utilizing a broad range of temperatures from 25°C - 240°C. Each dish was weighed daily until there was no change in weight, signifying that the remaining water had been evaporated from the sample.

Similarly, seven variable pH samples were made using a similar procedure as that of the variable temperature samples.  In this set of experiments, each sample consisting of 5.00 g of precipitated silica was added to approximately 125 mL of milli-Q water, instead of 225 mL, so as to shorten the time required to filter each sample.  These samples were also kept on a shaker before analysis to keep the silica from settling or turning into a gel.  Each sample was then titrated with HCl and/ or NaOH until a desired pH of 2.5, 4.5, or 8.5 was achieved.  The variable-temperature samples were used for the pH 6.5 level.  The samples were allowed to rest on the shaker for at least one day so each solution could come to equilibrium.  The pH level of each sample was measured and recorded just prior to the filtering process.  The samples were vacuum-filtered through 0.1 μm filters and then were dried in open glass dishes in ovens set to 60°C, 120°C, and 180°C.  The dishes were weighed daily until no change in weight was detected.

The BET method is the accepted method of measuring the specific surface area of precipitated silicas.  This method uses a relationship between the rate of condensation of nitrogen gas on a sample's surface and the rate of evaporation to indicate the total surface area.[2]  For this project, a Micromeritics Gemini II 2370 Surface Area Analyzer was used.  A pre-formatted procedure was utilized including a 2.0 minute evacuation time, a 3 second equilibration time, saturation pressure that was measured each day, and an evacuation rate of 250.0 mm Hg/min.  Each sample took approximately 40 minutes to run.  The dried samples were analyzed using the BET method three times each and an average value was determined.  An instrument calibration sample was performed at the start and conclusion of the entire silica analysis.

Results

According to specifications from the Degussa Corporation, their Ultrasil® VN3SP Powder synthetic amorphous precipitated silica has a BET Surface Area of 155-195 $m^2$/g, a pH of 5.6-7.0, is about 98% $SiO_2$, has an average agglomerate size of 100 μm, and its primary function is for reinforcement.[4]  The analysis of the silica powder straight from the container was 119.7 $m^2$/g before oven drying and 133 $m^2$/g after oven drying at 60°C.

Table A13.4-1 contains the data collected for the temperature-treated samples. Each of the three BET surface area values along with the average of each sample is included.  These data are plotted in Figure A13.4-1.

**Table A13.4-1**. Temperature-Treated Samples

| pH | Temp °C | Surface Area (m²/g) | | | |
|----|---------|-------|-------|-------|---------|
|    |         | Run 1 | Run 2 | Run 3 | Average |
| 6.54 | 25 | 127.0893 | 127.6722 | 128.1877 | 127.6497 |
| 6.56 | 40 | 131.5978 | 131.3754 | 131.6898 | 131.5543 |
| 6.56 | 60 | 134.5928 | 135.1595 | 135.2980 | 135.0168 |
| 6.59 | 70 | 138.1242 | 138.1563 | 138.2336 | 138.1714 |
| 6.55 | 80 | 142.1936 | 142.1401 | 142.2526 | 142.1954 |
| 6.57 | 90 | 143.3452 | 143.7177 | 143.7998 | 143.6209 |
| 6.67 | 100 | 141.3027 | 141.3854 | 141.3778 | 141.3553 |
| 6.52 | 110 | 146.9735 | 147.0384 | 147.0337 | 147.0152 |
| 6.58 | 120 | 144.8748 | 145.0693 | 145.0400 | 144.9947 |
| 6.57 | 130 | 144.4004 | 144.4707 | 144.4081 | 144.4264 |
| 6.59 | 140 | 141.7958 | 141.7267 | 141.7095 | 141.7440 |
| 6.60 | 150 | 144.5077 | 144.6039 | 144.6881 | 144.5999 |
| 6.62 | 160 | 147.5660 | 147.6225 | 147.6285 | 147.6057 |
| 6.52 | 180 | 145.2537 | 145.3810 | 145.4996 | 145.3781 |
| 6.53 | 200 | 147.6981 | 147.5629 | 147.5582 | 147.6064 |
| 6.57 | 220 | 148.2259 | 148.4143 | 148.5234 | 148.3879 |
| 6.55 | 240 | 149.4955 | 149.5353 | 149.6313 | 149.5540 |

**Effect of Temperature on Surface Area**



The equation shown on the graph:

$$y = 96.231 + 22.676\log(x) \quad R = .97201$$
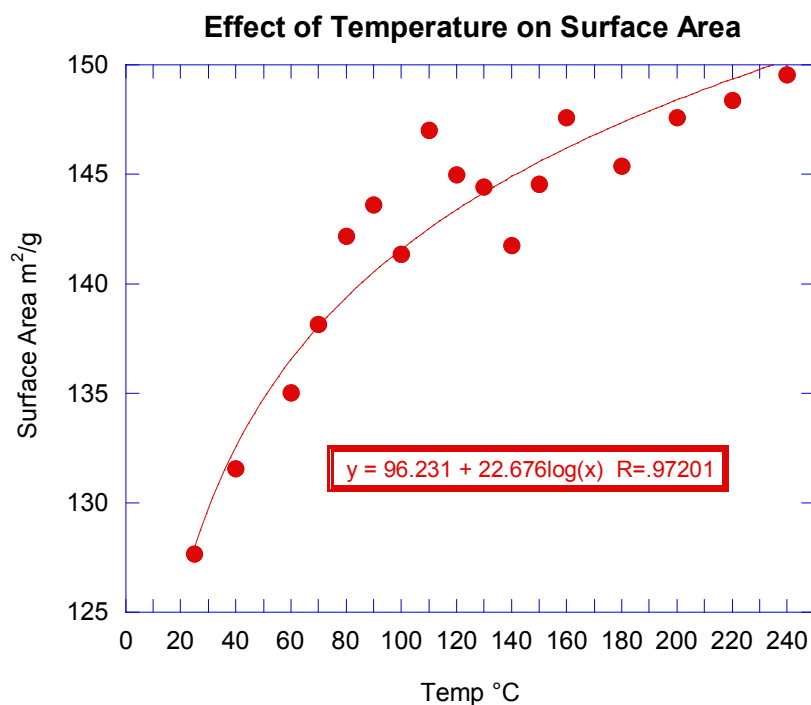
**Figure A13.4-1**. The relationship between temperature and the resulting surface area

Table A13.4-2 contains the data of the pH-treated samples. It records the pH, temperature, and surface area values of each sample. These data are represented in Figure A13.4 -2 where it's apparent that the two pH curves parallel the trend of the initial pH 6.6 curve.

**Table A13.4-2**. pH-Treated Samples

| pH | Temp °C | Surface Area sq. m/g | | | |
|---|---|---|---|---|---|
| | | Run 1 | Run 2 | Run 3 | Average |
| 2.495 | 60 | 131.8429 | 131.7842 | 132.1423 | 131.9231 |
| 2.502 | 120 | 138.6475 | 138.7264 | 138.9497 | 138.7745 |
| 2.456 | 180 | 142.0556 | 142.0239 | 142.1106 | 142.0634 |
| 4.867 | 120 | 139.5446 | 140.0336 | 140.3531 | 139.9771 |
| 7.707 | 60 | 130.9349 | 131.0528 | 131.1445 | 131.0441 |
| 7.933 | 120 | 135.3619 | 135.6808 | 135.9116 | 135.6514 |
| 7.867 | 180 | 137.9254 | 137.9863 | 138.0351 | 137.9823 |

**Effect of Temperature and pH on Surface Area**

Legend:
- pH 2.5
- pH 4.9
- pH 6.6
- pH 7.8

$y = 93.952 + 21.415\log(x)$   R= 0.99875
$y = 95.041 + 22.947\log(x)$   R= 0.94245
$y = 105.1 + 14.624\log(x)$   R= 0.99931

Y-axis: Surface Area $m^2/g$
X-axis: Temp °C
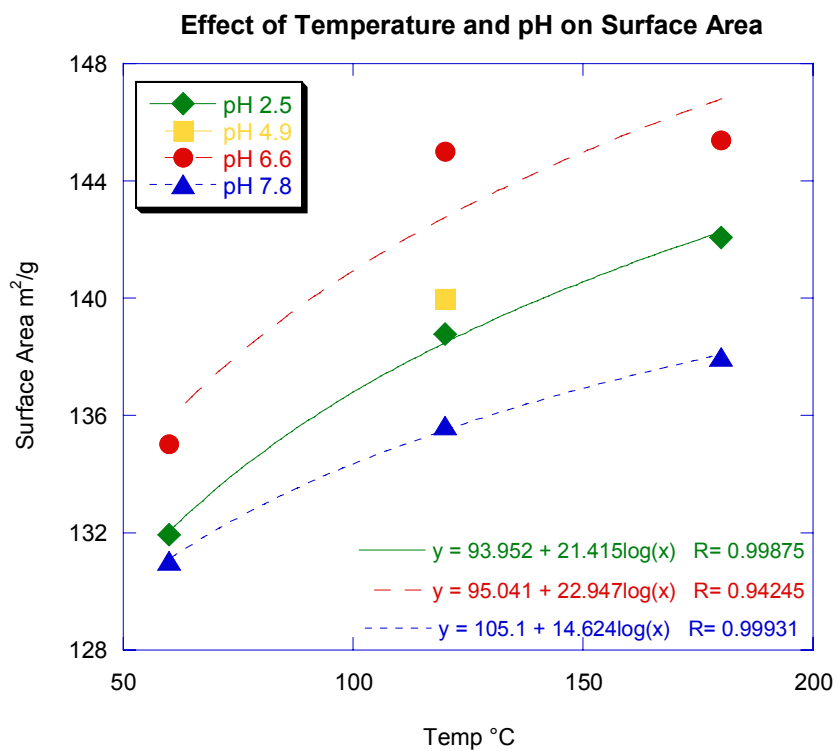
**Figure A13.4-2**.  The relationship between the pH level of the silica in solution and the resulting surface area after being oven dried

Discussion, Conclusions, and Future Work

Figure A13.4-1 suggests that drying temperature has an effect on surface properties.  It appears to follow a logarithmic trend producing lower surface areas at lower temperatures and higher surface areas at higher temperatures.  This effect may be due to the rapid evaporation of water at temperatures exceeding 100°C.  The lower surface areas achieved at lower temperatures may be due to residual moisture remaining in some of the silica pores; at lower temperatures such moisture would be less likely to evaporate.

As illustrated in Figure A13.4-2, the logarithmic relationship between surface area and oven temperature appears be independent of pH.  Considering the pH effects only, it appears that the surface properties were strongly affected by the acid and base treatments.  At lower pH values, the surface area estimates are lower than the original precipitates, and the same is true for samples equilibrated with a pH higher than the original samples.  One factor possibly affecting the surface area at higher pH levels is the reverse

solubility of silica that might cause some of the silica to dissolve at pH levels higher than 6.6.

Freeze drying was investigated as an alternative drying option, and was found to be ineffective for commercial and industrial use.  Other drying methods could be considered along with the resulting differences in the produced silica.  A brief investigation into vibrational spectroscopies was also initiated but was abandoned for lack of time.  This would have incorporated the use of Raman scattering to identify changes in the structure of the silica due to the drying process.  NMR and IR could also be used to further explore the effect and magnitude of any structural changes to the silica due to the drying process.

### *References*
[1]  PPG Industries Silicas. INTERNET.
http://corporate.ppg.com/PPG/SBU/Silicas/default.htm 07/15/03.
[2]  CalEnergy Operating Company. "The Silica Project." May 1998, Page 6.
[3]  Timothy A. Okel and Walter H Waddell, Rubber Chemistry and
      Technology 68 (1995) 59.
[4]  Degussa. INTERNET. http://www.degussa.com/en/products.html
      07/15/03.

13.5 <u>Appendix - Results of tests of physical properties of rubber fabricated using geothermal silica as filler (from Byers Rubber Consulting).</u>

(*The work described here relates to Subtask 2.1.3 of PIR-00-003*.)

Attached are an e-mail and documents that provide the results of rubber tests using geothermal silicas and other reference silicas.

<u>E-mail from John Byers to William Bourcier, December 2004.</u>

Bill,

I have attached an Excel file with the data from the evaluation of the silica samples MA-1104-1, MA-1104-2 and MA-1104-3. The file should be set-up to print only the data sheet of the worksheet.

My observations:

Sample MA-1104-2 was slightly more reinforcing than MA-1104-1, but both performed like a clay filler rather than a silica. They gave a stiffening effect, but did not enhance the strength of the polymer-filler mixture (tensile strength, abrasion resistance).

Sample MA-1104-3 was very reinforcing. It gave high tensile strength, good abrasion resistance and a slower cure rate -- like a fairly high surface area silica.

The HiSil 233 that was included as a reference gave typical results for a 140-150 sq.m/gram surface area standard commercial silica. It did not reinforce as well as MA-1104-3 (tensile and abrasion loss), but was well above samples MA-1104-1 and MA-1104-2.

Conclusion:
If sample MA-1104-3 was produced from your process, then it appears that you have developed a successful process. The other two samples would not be marketable fillers for rubber compounds.

Please reply with your comments. It looks like this wraps up the project for this year.

Best regards,

John Byers
Byers Rubber Consulting, Inc.
902 Devonwood Dr.
Wadsworth, OH 44281-8860

**Table A13.5-1**.  February 2003 Test Data:

**ORDER TABLE**

ORDER:      BRC-025
DATE:       2-26-2003
Title:         BRABENDER SBR - Silica Sample Evaluations

| Min | CURE MB (BRABENDER) | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 10.0 |
| 1' | Zinc Oxide | 3.0 |
| " | Stearic Acid | 2.0 |
| " | Carbowax 3350 | 1.0 |
| " | RM Sulfur | 2.0 |
| " | Santocure NS | 1.5 |
| " | TMTM (Unads) | 0.5 |
| 4' | DUMP | 20.0 |

| Min | BRABENDER MAIN MIX: | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 90.0 |
| 1' | SILICA | 35.0 |
| 4.5' | CURE MB | 20.0 |
| 6' | DUMP | 145.0 |

TESTS:      MDR @ 150 C            D2084

CURE:      150 C
             (NOTE:  Use approx. t90% + 10')

STRESS/ STRAIN, ORIG.:         D-412     MODULUS @ 100%, 200%, 300%

HARDNESS:                  D-2240

PICO ABRASION:           D-2228    @ 23 C
             [NOTE:  Rebound, Pendulum (Zwick) @ 23 C on Pico Button]

| Compound # | Silica Samples |
|-----------|----------------|
| 1 | VN3 SP |
| 2 | MA-1203-1 |

**BATCH TABLE**

ORDER: BRC-025
DATE: 2-26-2003
Title: BRABENDER SBR - Silica Sample Evaluations

| Compound # | Silica Samples |
|---|---|
| 1 | VN3 SP |
| 2 | MA-1203-1 |

**OIL BATH TEMPERATURE: 45 C**

| Min | CURE MB (BRABENDER) | grams | 60 RPM | FACTOR = | 3.7 |
|---|---|---|---|---|---|
| 0' | SBR 1502 | 37.0 | | | |
| 1' | Zinc Oxide | 11.1 | | | |
| " | Stearic Acid | 7.4 | Add Ingred. Slowly | | |
| " | Carbowax 3350 | 3.7 | | | |
| " | RM Sulfur | 7.4 | | | |
| " | Santocure NS | 5.6 | Pre-heat mill rolls to 120F | | |
| " | TMTM (Unads) | 1.9 | | | |
| 4' | DUMP | 74.0 | (Tight Mill. Roll and pass thru end-wise 4 times, sheet out, cool) | | |

| Min | BRABENDER MAIN MIX | | 60 RPM | FACTOR = | 0.6 |
|---|---|---|---|---|---|
| 0' | SBR 1502 | 50.4 | | | |
| 1' | SILICA | 19.6 | Add silica slow, put ram down. | | |
| 3' | scrape | | | | |
| 4.5' | CURE MB | 11.2 | (Ram down after adding Cure MB.) | | |
| 6' | DUMP | 81.2 | (Tight Mill. Roll and pass thru end-wise 4 times, sheet out, cool) | | |

... RECORD MIX ON CHART

...

|  | THICKNESS | WEIGHT (G) |
|---|---|---|
| MDR @ 150C | 0.300 | 5.0 |
| S/S Half Slab | 0.090 | 43.0 |
| PICO Button | ? | 22.0 |

**REPORT TABLE**

ORDER: BRC-025
DATE: 2-26-2003
Title: BRABENDER SBR - Silica Sample Evaluations

| Min | CURE MB (BRABENDER) | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 10.0 |
| 1' | Zinc Oxide | 3.0 |
| " | Stearic Acid | 2.0 |
| " | Carbowax 3350 | 1.0 |
| " | RM Sulfur | 2.0 |
| " | Santocure NS | 1.5 |
| " | TMTM (Unads) | 0.5 |
| 4' | DUMP | 20.0 |

| Min | BRABENDER MAIN MIX: | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 90.0 |
| 1' | SILICA | 35.0 |
| 4.5' | CURE MB | 20.0 |
| 6' | DUMP | 145.0 |

| COMPOUND: | | 1 | 2 | Previous data in this recipe: | | | |
|-----------|---|---|---|----------|----------|-------|----------|
| Silica: | | VN3 SP | MA-1203-1 | Ultrasil | Hubersil | HiSil | Ultrasil |
| Surface Area (m2/g) | | (na) | (na) | 175.0 | 135-150 | | 55.0 |
| **MD Rheom @ 150 C (302F)** | | | | | | | |
| ML | Min. Viscosity | 1.5 | 1.3 | 1.6-1.8 | 1.5-1.8 | 1.6 | 1.5 |
| tS1 | Induction Time | 4.8 | 1.5 | 3.0-3.8 | 2.8-3.6 | 3.0 | 3.9 |
| MH | Maximum Torque | 14.9 | 18.0 | 17.0-17.1 | 17.8 | 18.0 | 22.1 |
| CRI | Rate of Cure | 13.7 | 68.9 | 19.6-21.9 | 18.9-23.9 | 22.0 | 17.3 |
| t20% | Time - 20% Cure | 5.6 | 1.7 | 3.4-4.3 | 3.3-4.2 | 4.2 | 4.5 |
| t50% | Time - 50% Cure | 7.1 | 1.9 | 4.4-5.3 | 4.2-5.0 | 5.0 | 5.2 |
| t90% | Time - 90% Cure | 12.1 | 3.0 | 8.1-8.4 | 7.8-8.1 | 8.0 | 9.7 |
| | Cure Time @ 150C (min.): | 22' | 13' | 20' | 20' | 20' | 20' |
| **STRESS/STRAIN** | | | | | | | |
| 100% MODULUS (psi) | | 190.0 | 280.0 | 220-240 | 220-250 | 400.0 | 350.0 |
| 200% MODULUS (psi) | | 260.0 | 430.0 | 370-380 | 350-400 | 620.0 | 640.0 |
| 300% MODULUS (psi) | | 380.0 | 690.0 | 540-630 | 570-630 | 1080.0 | |
| TENSILE (psi) | | 2440.0 | 780.0 | 1740-2420 | 1490-1540 | 1780.0 | 840.0 |

| % ELONGATION | 650.0 | 320.0 | 530-570 | 460-480 | 380.0 | 270.0 |
|---|---|---|---|---|---|---|
| HARDNESS (Shore A) | 55.0 | 60.0 | 57-59 | 56-59 | 60.0 | 60.0 |
| | | | | | | |
| **ZWICK REBOUND @ 23C, %** | | | | | | |
| (Rebound on Pico Button) | 56.4 | 66.7 | 58.3-59.0 | 59.9-60.7 | 60.4 | 71.6 |
| | | | | | | |
| **PICO ABRASION** | | | | | | |
| Wt. Loss, mg | 45.7 | 89.1 | 42.6-44.5 | 43.5-48.1 | 50.0 | 78.6 |

**Table A13.5-2**.  December 2004 Test Data:

ORDER
TABLE

ORDER:      BRC-030
DATE:       11-11-04
Title:         BRABENDER SBR - Silica Sample Evaluations

| Min | CURE MB (BRABENDER) | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 10.0 |
| 1' | Zinc Oxide | 3.0 |
| " | Stearic Acid | 2.0 |
| " | Carbowax 3350 | 1.0 |
| " | RM Sulfur | 2.0 |
| " | Santocure NS | 1.5 |
| " | TMTM (Unads) | 0.5 |
| 4' | DUMP | 20.0 |

| Min | BRABENDER MAIN MIX | phr |
|-----|--------------------|-----|
| 0' | SBR 1502 | 90.0 |
| 1' | SILICA | 35.0 |
| 4' | CURE MB | 20.0 |
| 5.5' | DUMP | 145.0 |

TESTS:     MDR @ 150 C              D2084

CURE:      150 C
            [NOTE:  Use approx. t90% + 10']

STRESS/ STRAIN, ORIG.:          D-412     MODULUS @ 100%, 200%, 300%

HARDNESS:                D-2240

PICO ABRASION:           D-2228     @ 23 C
            [NOTE:  Rebound, Pendulum (Zwick) @ 23 C on Pico Button]
            [NOTE:  No Pico button on Compound 1]

| Compound # | Silica Samples |
|------------|----------------|
| 1 | 1104-1 |
| 2 | 1104-2 |
| 3 | 1104-3 |
| 4 | HiSil 233 |

BATCH
TABLE

ORDER:    BRC-030
DATE:     11-11-04
          BRABENDER SBR - Silica Sample
Title:    Evaluations

| Compound # | Silica Samples |
|---|---|
| 1 | 1104-1 |
| 2 | 1104-2 |
| 3 | 1104-3 |
| 4 | HiSil 233 |

 **OIL BATH TEMPERATURE:
45 C**

| Min | CURE MB (BRABENDER) | Weight (g) | | | |
|---|---|---|---|---|---|
| | | | | FACTOR | |
| | | | 60 RPM | = | 3.60 |
| 0' | SBR 1502 | 36.00 | | | |
| 1' | Zinc Oxide | 10.80 | Add Ingred. Slowly | | |
| " | Stearic Acid | 7.20 | | | |
| " | Carbowax 3350 | 3.60 | | | |
| " | RM Sulfur | 7.20 | | | |
| " | Santocure NS | 5.40 | Pre-heat mill rolls to 120F | | |
| " | TMTM (Unads) | 1.80 | | | |
| 4' | DUMP | 72.0 | (Tight Mill.  Roll and pass thru end-wise 4 times, sheet out, cool) | | |

| Min | BRABENDER MAIN MIX | Weight (g) | Compound 1 | | |
|---|---|---|---|---|---|
| | | | | FACTOR | |
| | | | | 60 RPM   =   0.54 | |
| 0' | SBR 1502 | 48.60 | 43.7 | | |
| 1' | SILICA | 18.90 | 17.0 | Add silica slow, put ram down. | |
| 3' | scrape | | | | |
| 4' | CURE MB | 10.80 | 9.7 | (Ram down after adding Cure MB.) | |

| 5.5' | DUMP | 78.30 | 70.4 | (Tight Mill. Roll and pass thru end-wise |

4 times, sheet out, cool)

... RECORD MIX ON CHART ...

|  | THICKNESS | WEIGHT (g) |
|---|---|---|
| MDR @ 150C | 0.300 | 5.0 |
| S/S Half Slab | 0.090 | 43.0 |
| PICO Button | ? | 22.0 |

REPORT TABLE

ORDER: BRC-030

DATE: 11-16-04

BRABENDER SBR - Silica

Title: Sample Evaluations

| Min | CURE MB (BRABENDER) | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 10.0 |
| 1' | Zinc Oxide | 3.0 |
| " | Stearic Acid | 2.0 |
| " | Carbowax 3350 | 1.0 |
| " | RM Sulfur | 2.0 |
| " | Santocure NS | 1.5 |
| " | TMTM (Unads) | 0.5 |
| 4' | DUMP | 20.0 |

| Min | BRABENDER MAIN MIX: | phr |
|-----|---------------------|-----|
| 0' | SBR 1502 | 90.0 |
| 1' | SILICA | 35.0 |
| 4' | CURE MB | 20.0 |
| 5.5' | DUMP | 145.0 |

| COMPOUND: | | 1 | 2 | 3 | 4 |
|-----------|---|---|---|---|---|
| Silica: | | 1104-1 | 1104-2 | 1104-3 | HiSil 233 |
| | | | | | |
| **MD Rheom @ 150 C (302F)** | | | | | |
| ML | Min. Viscosity | 1.1 | 1.1 | 1.6 | 1.6 |
| tS1 | Induction (Scorch Time) | 3.3 | 3.7 | 4.5 | 3.3 |
| MH | Maximum Torque | 18.9 | 16.8 | 15.5 | 17.6 |
| CRI | Rate of Cure | 20.0 | 26.8 | 14.2 | 27.1 |
| t20% | Time - 20% Cure | 3.7 | 4.1 | 5.1 | 3.6 |
| t50% | Time - 50% Cure | 4.3 | 4.7 | 6.7 | 4.4 |
| t90% | Time - 90% Cure | 8.3 | 7.5 | 11.5 | 6.9 |
| | Cure Time @ 150C (min.): | 18' | 18' | 22' | 17' |

| **STRESS/STRAIN** | | | | |
|---|---|---|---|---|
| 100% MODULUS (psi) | 244 | 346 | 239 | 273 |
| 200% MODULUS (psi) | 330 | ---- | 374 | 437 |
| 300% MODULUS (psi) | ---- | ---- | 583 | 677 |
| TENSILE (psi) | **348** | **520** | 1759 | 1502 |
| % ELONGATION at BREAK | 235 | 196 | 507 | 442 |
| HARDNESS (Shore A) | 59 | 59 | 60 | 63 |
| | | | | |
| **ZWICK REBOUND @ 23C, %** | | | | |
| (Rebound on Pico Button) | No Test | 74.0 | 65.9 | 64.8 |
| | | | | |
| **PICO ABRASION** | | | | |
| Wt. Loss, mg | No Test | **161.6** | 42.6 | 47.6 |